GAS PRODUCTION DURING PEAT DECAY

Thesis submitted for the degree of PhD

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To my parents,

who will appreciate the *real* worth of this.

With love and gratitude.

ABSTRACT

Decay and accumulation of blanket peat in the Northern Pennine region of England are considered, both in quantitative and qualitative terms. Productivity on the surface of these peat bogs is not unusually high, suggesting that a low decay rate may be responsible for the accumulation of the peat. Considerable study has formerly been made of the aerobic decay processes, at the expense of the parallel anaerobic processes, which have largely hitherto been considered negligible. Yet a current mathematical model of peat accumulation suggests that it is likely to be the *anaerobic* decay rate which determines the total depth of peat which may accumulate. Further, such models intimate that a very small absolute change in the anaerobic decay rate will have an unexpectedly large effect on the potential steady state depth of peat.

The present study concentrates on obtaining measurements of anaerobic decay rates, and on identifying the possible limiting environmental factors of the decay. The design of a sampler to collect gas samples *in situ* from blanket peat is described. The components of particular interest in the samples are CH_4 and CO_2. Gas concentrations down eight peat profiles at two sites are monitored over two seasons. Simultaneous surface flux measurements above pool, lawn and hummock microhabitats are also made. Water level, temperature, pH, redox potential, depth of the sulphide zone and total sulphide concentration are recorded on each field visit.

The results from the gas sample analyses are discussed in relation to the environmental factors and in relation to our present understanding of peat decay rates and their consequences on peat accumulation. The anaerobic decay rate is calculated, and is confirmed to be several orders of magnitude less than that in the overlying aerobic peat. It is shown that the methane is *not* fossil, but is continually being produced at all depths. Rates of gas *production* are calculated.

Annual methane and carbon dioxide losses from entire peat bogs are calculated to contribute a significant amount to carbon cycling, on a site-specific and global scale.

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CONVENTIONS AND ABBREVIATIONS

The following conventions and abbreviations have been adopted throughout, unless stated otherwise in the text.

CONVENTIONS

Depths - Depths (for example, of water level, sulphide zone, temperature measurements) are reported relative to a datum (for example, peat surface, bucket rim). That is, a negative value represents a point below the datum.

Water levels - Water levels are reported relative to the peat surface, unless stated otherwise. A positive value represents standing water.

Gas fluxes - Positive values represent an efflux of gas (as indicated by an increase in the concentration of the sampler contents): the peat system is acting as a source.

- Negative values represent an influx of gas (concentration of sampler contents decreases); the peat system is acting as a sink.
- Methane and carbon dioxide fluxes are reported as the mass of the carbon fraction (CH_4-C and CO_2-C).
- Values represent the *net* flux over the sampling period.

Significance levels of statistics - * $p<0.05$; ** $p<0.01$; *** $p<0.001$; ns $p\geq0.05$

ABBREVIATIONS

Garden Experiment

Pre I, I, II and III	The four stages of the Garden Experiment.
UP	Uncut (unclipped) Pool core
CP	Cut Pool (i.e. green surface vegetation removed)
UL	Uncut Lawn core
CL	Cut Lawn core
UH	Uncut Hummock core
CH	Cut Hummock core

CONVENTIONS AND ABBREVIATIONS

M1	Minibog 1
M2	Minibog 2

Field Monitoring

MH	Moor House National Nature Reserve
CR	Coom Rigg National Nature Reserve
UP, CP, UL, CL, UH, CH	Field sampling areas, as for Garden Experiment, above
CW	Cut Wet sampling areas at Coom Rigg
CD	Cut Dry sampling areas at Coom Rigg
Site	Moor House or Coom Rigg
site	An individual sampling area, enclosed by a bucket, or a cluster of such areas (for example, an individual bucket area at site 4-6, or the cluster of 6 buckets forming the 4-6 sampling site at MH)

Statistical Analysis

ANOVA	Analysis of variance
ANOVAs	Analyses of variance

CHAPTER 1

INTRODUCTION

... While from the bounded level of our mind,
Short views we take, nor see the lengths behind;
But more advanc'd, behold with strange surprize
New distant scenes of endless science rise!

Pope, *An Essay on Criticism*

INTRODUCTION

1.1 PEAT SYSTEMS

Peat is the accumulation of dead plant material. It accumulates in wet conditions, and so occurs in different situations in different climatic zones. In the Tropics it is restricted to coastal areas and the cool, wet mountain zones. In cooler, more humid, temperate regions peat systems are more extensive at intermediate altitudes, and vast tracts of relatively low land (300 m) may be peat-covered. The lower temperatures and broader spread of precipitation over the year allow peat to develop in valleys and small basins well inland, where other conditions for peat accumulation are satisfied. In the Arctic and Antarctic, with their extremes of cold weather broken only briefly by a 6-12 week season in which plant growth is possible, peat accumulates over all areas which are sufficiently poorly-drained and which therefore retain much of the (low) precipitation. Permafrost is important in this respect, and of course affects ground temperature as well as being a result of it. In the polar regions peat does not form on coastal land where ice-scouring occurs for much of the year. Neither do the frost-shattered mountain tops accumulate peat; they are too dry and exposed, if not too steep.

There are almost as many estimates of the amount of peat as there are articles dealing with the question. The reasons for the discrepancies lie not only in the fact that many peatlands are in remote locations, resulting in omission (or crude estimates) of area, but in the diversity of the definitions used to delimit the areas which should or should not be included in the assessment (for example, see papers in Tibbets 1968; Kivinen, Heikurainen & Pakarinen 1979 and Kivinen & Pakarinen 1981). Further, in deriving estimates of the *amount* of organic matter, or carbon, or the calorific value of the peat, in most cases workers do not state the basis on which their calculations are made; for example, the mean depth of peat assumed over the measured (or estimated) area, the bulk density of the peat, or the calorific conversion. It is therefore not possible to determine which estimate is the more accurate, as more areal (or other) surveys are added, or earlier ones improved. Tibbets (1968) estimated 150 x 10^6 ha to be peat covered, Olenin (1968) 118 x 10^6,

Moore & Bellamy (1974) 230 x 10^6 and Kivinen & Pakarinen (1981) 422 x 10^6 ha. The latter value includes all peat of 30 cm depth or more, and also drained peatlands, but not the full amount of tropical and arctic peatlands. The area estimates quoted here represent 1-3% of the total land surface of the earth (148.8 x 10^6 km^2, Tennent 1971). Bramryd (1979) states that Olenin (1968) estimated the global amount of carbon held in peat to be 160 Gt, whereas Clymo (1984) calculated a value of 180 Gt dry mass of carbon from figures in the same (Olenin) paper. Thus discrepancies can arise from a single set of figures. Kivinen & Pakarinen (1981) estimate the world's peat resources to be 400 Gt. This is at 40% moisture content, so assuming a conversion factor of 0.4 for carbohydrate (CH_2O) to carbon content. this is equivalent to 160 Gt dry mass of carbon. The amount of carbon held in terrestrial 'humus' (including peat) is estimated at 1000-3000 Gt (Woodwell *et al* 1978). By comparison, Whittaker (1975), citing Lieth & Whittaker (1975), gives the world terrestrial net primary productivity as 115 Gt y^{-1} (≡ 46 Gt y^{-1} C).

Thus it is clear that whatever the exact area of the world covered by peat, it is large and widespread, though there is a bias towards the northern hemisphere, and five countries (USSR, Canada, USA, Indonesia and Finland) account for about 95% of the world peatland area (Kivinen & Pakarinen 1981). The USSR is frequently quoted to have the largest proportion of peatland in any one country (e.g. Olenin 1968), but these calculations are based on the area of *exploitable* peat, and exclude much of Canada's peatlands. Kivinen & Pakarinen, adjusting for these underestimates of total peat area, arrive at an equal area of peat (150 x 10^6 ha) in the USSR and Canada. Thus together, these two have over 70% of the world's peatland area. Peat resources in the UK are estimated at 1.6 x 10^6 ha (Robertson & Jowsey in Tibbets 1968), or about 7% of the land area. The same authors calculate the UK peat resource to be 2.5 Gt. Of this, Scotland has the largest area (0.8 x 10^6 ha), followed by England, with about 0.4 x 10^6 ha, but Scotland and N. Ireland have the largest proportional cover in the UK: >10% and >12%, respectively. In Scotland this amounts to about 0.5 Gt C (1.2 Gt dry peat), compared with about 0.4 Gt C (1.0 Gt dry peat) in England and Wales combined.

These estimates include all peat types, from basic (soligenous) peat commoner in lowland areas and valleys to the acidic ombrogenous peat which covers most of the upland areas. Of the (UK) ombrogenous peat, blanket bog is the most widespread. In Scotland, with a total land area of about 8 x 10^6 ha (Taylor 1983), about 10% is covered by blanket bog (Robertson 1968). This is calculated assuming a minimum depth of 30 cm. If the minimum depth is increased to 60 cm, there are about 650 x 10^3 ha (≈8% of the land area). Locally, blanket bog may cover more than 80% of the land surface to an average depth of 2 m, for example on the Isle of Lewis.

Thus, although in many cases the basis of the calculations is unclear and many of the values are not directly comparable, it is clear that in Britain peat covers a large area of land, and that blanket bog is of particular importance in terms of cover and the mass of carbon held in it.

Peat is mainly organic matter. The exact distinction between peat and highly humic mineral soils is arbitrary and differs according to purpose: it is usually ‹20% dry weight as non-combustible inorganic 'ash', and may be as little as 1-2% in some (*Sphagnum*) peats. Peat is a rich energy source, and is exploited as such in the USSR, Finland and Ireland. Olenin (1968) states that exploitable peat reserves in the USSR amount to 71.5 x 10^6 ha, or 158 Gt. This represents 95.7% of the world's peat production. Second in rank order in this respect is Ireland (Eire), which accounts for 2% of total production (Robertson & Jowsey, in Tibbets 1968). Thus, apart from its importance as a major world ecosystem in terms of its area, it is important as a resource, and not just as one of fuel. In Great Britain it is used as fuel only by individuals in marginal communities, especially in the north and west of Scotland, but it is exploited commercially on a large scale for, in particular, the horticultural industry. There are numerous other reasons why an understanding of peat *per se*, and its formation, is important. Workers in the fields of palaeoecology, engineering, medicine and welfare, chemistry, horticulture and agriculture, amongst others, all have a need for more information relating to peat to enable them to use the resource more efficiently. It is also important that they should understand its limits so that over-

exploitation, and possible irreversible damage, is avoided. More recently the rôle of peat deposits in the world carbon budget has been examined (e.g. Woodwell *et al* 1978; Bramryd 1979).

The major peat type in Britain is upland ombrogenous peat, and specifically, upland blanket peat. It occurs as an extensive covering over flat, or only gently sloping, impermeable ground, where the annual rainfall is high (>1300 mm y^{-1}) and well spread over the year (Birks & Birks 1980, p.48). Such conditions are found in the north and west of Britain, above about 350 m where the mean annual temperature is about 5°C and the mean annual rainfall often 2000 mm or more. Here the peat is typically 2-3 m deep. In basins, kettle-holes or valleys at a range of altitudes, different types of peat accumulate, and may reach depths of 5-6 m or, exceptionally, 8 m. Outside Britain there exist peat deposits of many sorts, some of which are an order of magnitude deeper than those already referred to, for example near Padul, Spain where alternating bands of peat and lake marl reach a depth of 72 m (Florschütz, Menèndez Amor & Wijmstra 1971).

The present study aims to contribute towards an understanding of peat accumulation, particularly the rôle of anaerobic decay, which has been neglected or, at best, underestimated, by the majority of workers, as an important factor in the peat accumulation process and its limits. The study is confined to the consideration of acid, ombrogenous peat in the Northern Pennine hills. Details of the peat types and field sites used are given in Chapter 2.

1.2 MODELLING PEAT ACCUMULATION

Peat accumulates when productivity exceeds the rate of decay. 'Decay' here and throughout refers to the loss of mass, and does not necessarily infer any specific change in the physical or chemical nature of the peat, though such changes occur, and are responsible for the mass lost over the peat profile.

Productivity adds material at the surface each year at rates (net, dry weight) estimated to be between 491 and 868 g m^{-2} y^{-1} (≡ 196 to 347 g m^{-2} y^{-1} C) (Forrest & Smith 1975) for blanket bog sites

within the Moor House National Nature Reserve (MH). Estimates for the area of the Reserve which was used for the present study (Burnt Hill pool and hummock complex (BH)) are as follows: *Sphagnum* spp 90 g m^{-2} y^{-1} (≡ 36 g m^{-2} y^{-1} C), other (vascular) species 273 g m^{-2} y^{-1} (≡ 109 g m^{-2} y^{-1} C) (Clymo & Reddaway 1971). The values are lower than those quoted above from Forrest & Smith because Burnt Hill is a wet site and has a higher cover of *Sphagna* at the expense of the vascular species. The productivity of *Sphagnum* varies with species and microhabitat (Clymo 1970; Clymo & Reddaway 1971). It is instructive to compare these values with some from other ecosystems in Britain and elsewhere. Chapman (1965) gives 77 g m^{-2} y^{-1} (≡ 30.8 g m^{-2} y^{-1} C) for *Sphagnum* (*S. magellanicum* and *S. papillosum*) at Coom Rigg Moss (see Chapter 2). Productivity of two International Biological Programme (IBP) tundra sites (MH is a third) are estimated to be 206 g m^{-2} y^{-1} (Stordalen mire, Sweden; 68°N, 19°E, altitude 351 m; Rosswall *et al* 1975) and 230 g m^{-2} y^{-1} (Barrow coastal tundra, Alaska; 71°N, 156°W, altitude 0 m; Miller *et al* 1980). At Barrow 162 g m^{-2} y^{-1} was attributable to vascular species, 6 g m^{-2} y^{-1} to mosses, and <1 g m^{-2} y^{-1} to lichens. Summers (1978) gives the areal productivity of a bryophyte-rich, *Calluna*-dominated mixed heath in the Cairngorm mountains, UK (altitude 915 m) as 300 g m^{-2} y^{-1}, and that of a southern UK (Dorset) *Calluna*-dominated dry heathland as 320 g m^{-2} y^{-1}. According to Krebs (1972) *Sphagnum* bogs supporting forest have a productivity of 340 g m^{-2} y^{-1}, and Whittaker (1975, citing Lieth & Whittaker (1975)) gives a value of 600 g m^{-2} y^{-1} for temperate grassland.

Hence it is clear that the productivity of upland bogs in Britain is not exceptionally high, so it is reasonable to assume that decay must be slow if peat is to accumulate, as it does. That decay occurs is not doubted, and a rough measure of how much of the original mass is lost can be obtained through a very simple calculation. Assuming productivity to be 200 g m^{-2} y^{-1}, no decay, and peat bulk density, ρ, to be 0.1 g cm^{-3} (Clymo 1983 and Fig. 2.4, p.56), after 5000 years the accumulated peat would be 10 m deep, which is exceptional in Britain. It is clear, then, that much of the original mass must be lost, over time, through decay.

INTRODUCTION

Early formal descriptions of peat decay (e.g. Woodwell & Marples 1968 and Baker 1972) assumed that the rate of loss of mass was a constant proportion of the original mass, i.e. that the relationship between remaining mass and time was linear:

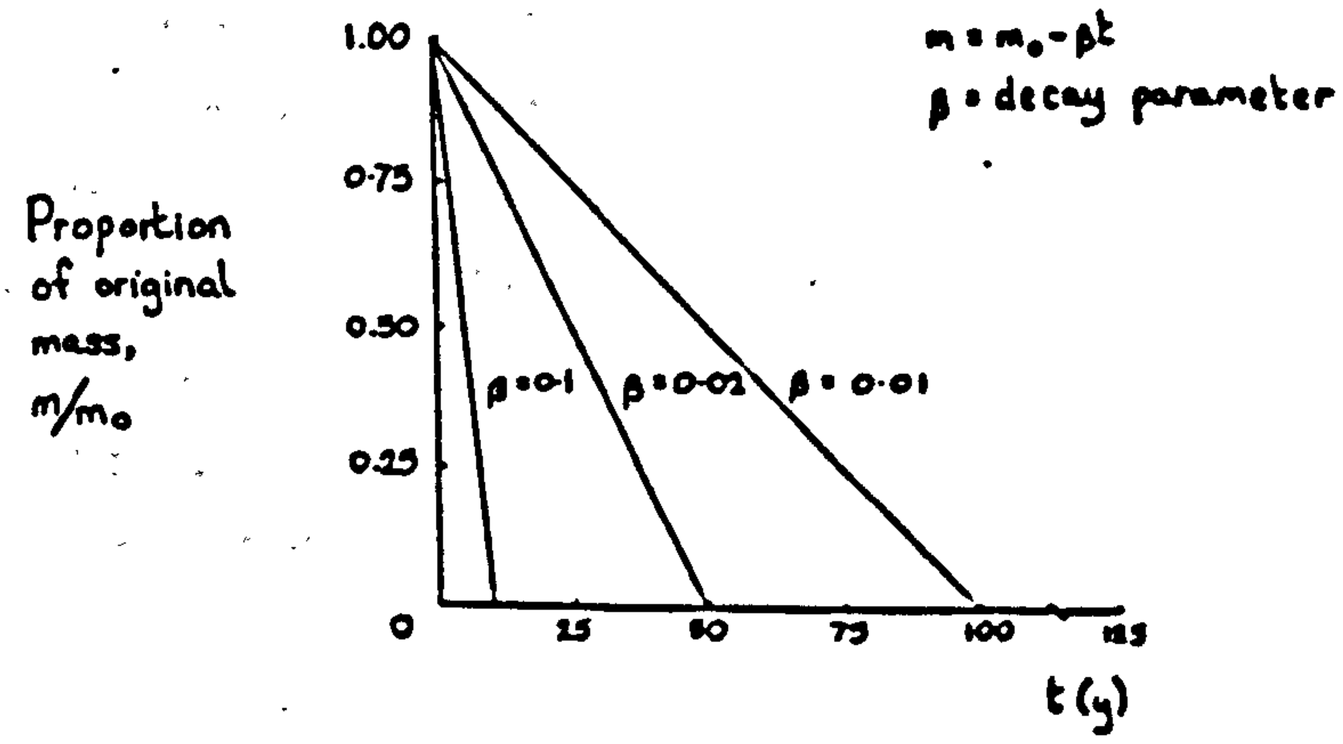
$$\frac{dm}{dt} = -\beta \qquad (1)$$

where m is the mass at time t and β is the decay parameter, which in this model has dimensions MT^{-1}. The solution to this is

$$m = m_0 - \beta t \qquad (2)$$

from which it follows that there is no peat remaining after a time period equal to m_0/β. Fig. 1.1 illustrates the model using a realistic range of (aerobic) decay parameters. It implies that all

FIG. 1.1 Linear decay model



the original material will have disappeared after 10 y for a mass of peat decaying at a rate of 0.1 y^{-1}, or after 100 y if decaying at a rate of 0.01 y^{-1}. Clearly, the model does not account for the majority of bogs in Britain which have accumulated more than a metre of peat and which are known to be thousands of years old at the base. Another description of decay was proposed by Jenny, Gessel & Bingham (1949); it follows an exponential course:

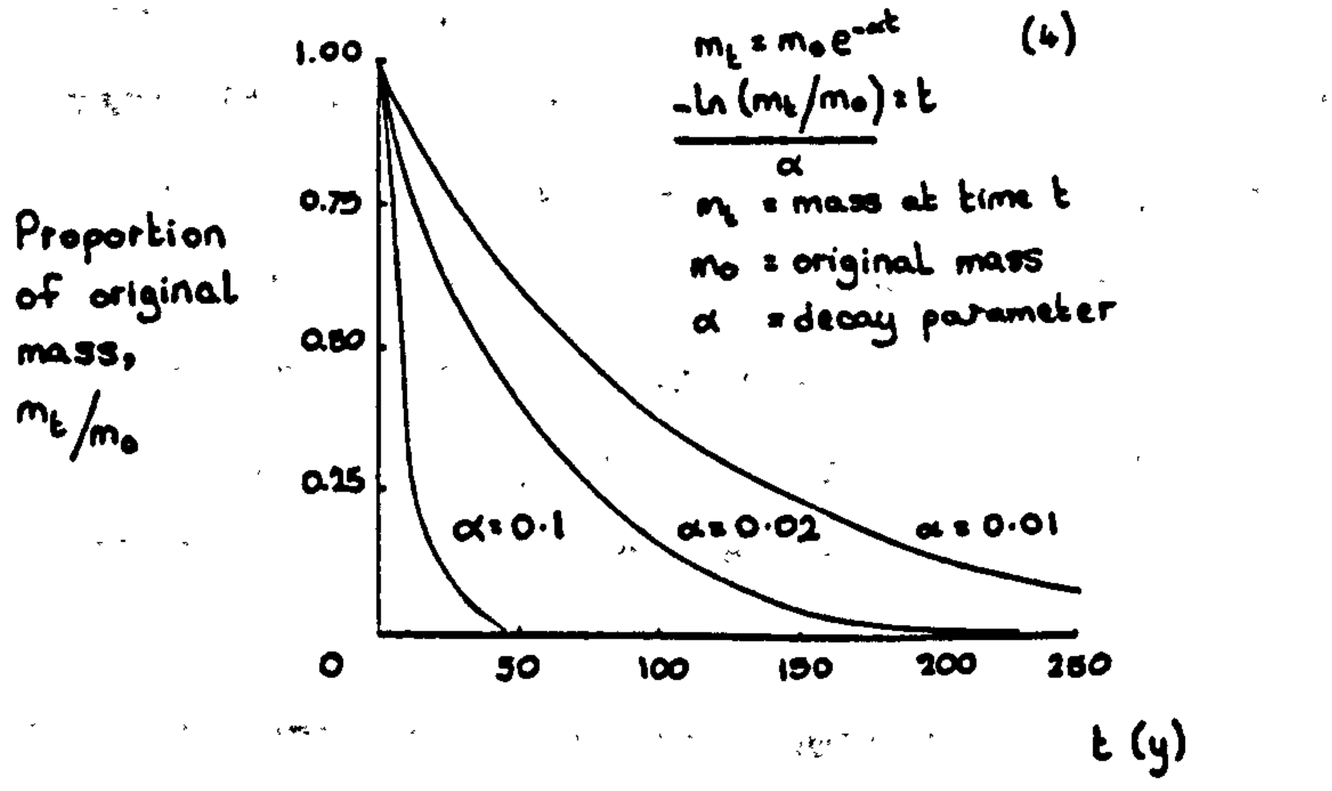
$$\frac{dm}{dt} = -\alpha m \qquad (3)$$

where m is the accumulated mass of peat at time t and α, the exponential decay parameter, has dimensions T^{-1}. According to this model, mass is lost at a constant proportional rate of the remaining mass. It makes two other assumptions: that decay is continuous, and that any annual, or other short-term, fluctuations in decay rate are insignificant compared with any long-term trends; that is, decay can be regarded as constant. The solution for m to equation (3) is

$$m_t = m_0 e^{-\alpha t} \qquad (4)$$

and shows that this model allows for the continued existence of some material. The plot becomes a straight line if the dependent axis, the mass at time t, is logarithmically scaled. Equation (4) may be rearranged so that the proportion of the original mass remaining after various periods can be calculated for a range of values of α. This has been done (Fig. 1.2) for the same three decay parameter values as were used in Fig. 1.1. Such a description has been favoured as the less incredible of the two (for a fuller treatment of the mathematics

FIG. 1.2 Exponential decay model



and assumptions of the model, see Olson 1963), and has been incorporated into the models of numerous workers investigating decay

in various ecosystems since its formulation (e.g. Gore & Olson 1967; Clymo 1978, 1984; Jones & Gore 1978). (Wieder & Lang 1982 give a basic mathematical description of the linear, exponential and other models and an appraisal of their goodness-of-fit to biological theory and observations.) Clymo (1983, 1984) tested the relative accuracy of the linear and exponential decay models using the field data of Baker (1972) from *Chorisodontium aciphyllum* banks in the maritime Antarctic, and those of Heal, Latter & Howson (1978) from decay experiments on various vascular plant species at MH in the Northern Pennines. Over the time periods (≤40 years) and the depths (≤45 cm) involved in these studies, Clymo found that both models gave reasonable fits to the data, accounting for upward of 67% of the variation. Indeed, in seven out of eight results the figure was at least 87% (Fig. 3, 1984). However, the comparison of the two models was continued for an extended time period until more than half the original mass had decayed and it was clear that the models diverged somewhere beyond the relatively short time period, and beyond about 50% loss of mass, which have so far been followed experimentally. It was concluded that, given the increase in bias in the experimental methods (loss of mass from buried litter bags at MH and moss increment methods in the Antarctic) which inevitably occur with prolonged experimental periods, that such experiments are unlikely to provide sufficiently accurate data for a reliable choice to be made. Although such a choice may be unimportant when short time periods are involved (<50 y), when concerned with modelling the course of decay over periods applicable to peat bog development (measured in hundreds or thousands of years), the choice *is* important. Because material at the base of so many peat bogs is known to have survived for thousands of years since it was initially incorporated at the surface, I have chosen to accept the exponential model of decay, and later in the present chapter the description will be tested further as part of a peat accumulation model.

It has already been stated that peat accumulation results when the rate of addition of material exceeds that of decay. Accepting the exponential decay model set out in equation (3), this can be expressed formally as

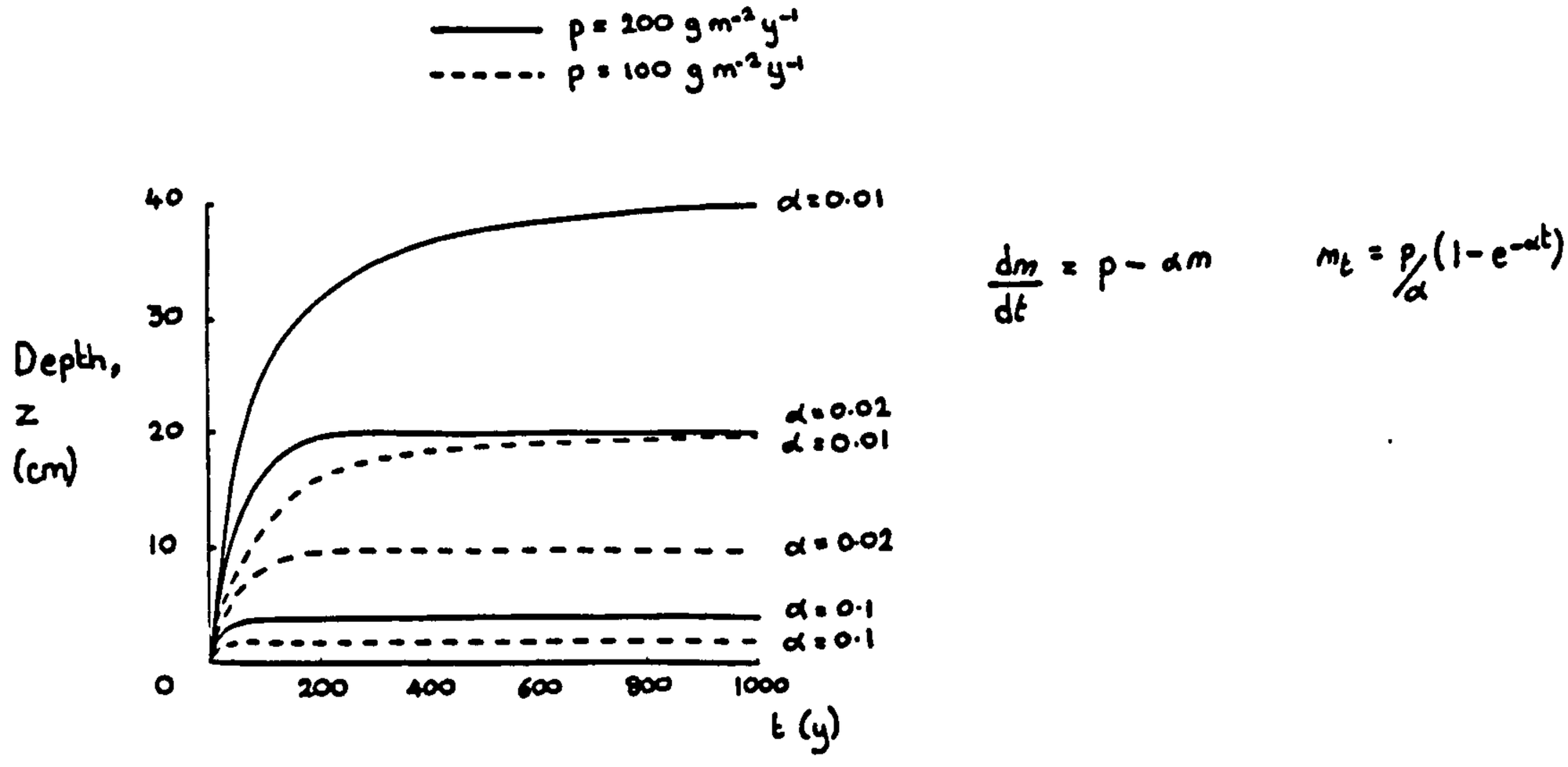
$$\frac{dm}{dt} = p - \alpha m \qquad (5)$$

where p is the net productivity ($ML^{-2}T^{-1}$). As for the decay component, productivity is assumed to be continuous and constant. The solution for m to equation (5) is

$$m_t = \frac{p(1-e^{-\alpha t})}{\alpha} \qquad (6)$$

and is plotted in Fig. 1.3 for two different values of p and the same values of α as were used for Fig. 1.2. Mass, m, is plotted as depth,

FIG. 1.3 Peat accumulation model



assuming a bulk density of 0.05 g cm^{-3} for the whole profile. Several consequences of equation (5) are now clear. First, peat does not accumulate indefinitely, but moves asymptotically towards a steady-state mass measured by p/α. Formally,

$$\text{as} \quad t \Rightarrow \infty, \qquad \text{then} \quad m_t \Rightarrow p/\alpha. \qquad (7)$$

Second, for a given rate of addition of dry mass the steady-state mass is indirectly proportional to the decay rate, so that a small absolute change in α, say from 0.02 to 0.01 y^{-1}, will result in a large (in this example two-fold) increase in the steady-state depth. In contrast to this, for a given rate of decay the steady-state mass

changes in direct proportion to the productivity, so that a two-fold increase is achieved by a two-fold increase in productivity. Third, the rate of peat accumulation in a bog which is close to a steady-state is very low, almost zero, and this is so *whatever the productivity.* Thus, a bog in a steady-state may be adding considerable mass to its surface layers and will assume a healthy, 'growing' appearance, but the net accumulation is roughly zero because the net productivity is matched by the loss of mass by decay from the underlying body of peat. Indeed, it is not necessary to restrict such a finding to the situation in bogs which are assumed to have reached a steady-state mass. By rearrangement and substitution into equation (6) it is possible to show that the proportion, Q, of the steady-state mass which has accumulated by the time t_ω is independent of productivity:

$$Q = \frac{m_t}{(p/\alpha)} = \frac{m_t\alpha}{p}$$

Equation (6) may be written

$$\frac{m_t\alpha}{p} = 1 - e^{-\alpha t}$$

Substituting in Q and t_ω for $m_t\alpha/p$ and t gives

$$Q = 1 - exp(-\alpha t_\omega) \qquad (8)$$

or

$$t_\omega = \frac{-\ln(1-Q)}{\alpha}. \qquad (9)$$

So the fourth consequence of equation (5) is that the time needed to reach a given proportion of the steady-state mass is independent of the productivity, and depends on the decay rate. This is evident from a closer inspection of Fig. 1.3.

According to the model of peat accumulation proposed in equation (5), then, the decay rate is important in determining the potential

total mass of peat that may develop, and is the sole parameter in determining the rate at which the final steady-state mass is reached.

For the range of values of p and α used for Fig. 1.3, the maximum steady-state depth attained, assuming bulk density to be 0.05 g cm^{-3}, was 40 cm. If the peat accumulation model on which these calculations are based, given in equation (5), is a reasonably accurate description of the processes involved, how are these steady-state depths to be reconciled with the fact that so many bogs are several metres deep? The answer lies in the nature of the peat itself. So far it has been assumed that a peat bog is a single component system which has a uniform structure and which behaves according to the same laws throughout its bulk. This is of course an over-simplification.

Mass is added at the surface (productivity) and after a period of time this material dies and begins to decay. New material continues to be added above. As the dead material decays it eventually begins to lose its structure and with this, its ability to support the ever-increasing mass of material above. So it collapses, and the interstitial spaces are significantly reduced in size; the bulk density increases. Above this zone of collapse the peat structure is relatively open and hydraulic conductivity is high, but below it the gaps between the fragments of the peat material are small and hydraulic conductivity is low. When precipitation falls, the water level rises and although it readily drains away through the open, uppermost layer of peat, its movement through the zone below the collapse is very slow. Thus the water level moves upward with, but lags behind, the bog surface. The newly-inundated peat rapidly becomes anoxic because as the dissolved oxygen is utilised in respiration it cannot be fully replaced by diffusion from above: the diffusion rate of oxygen in water is only about 10^{-4} that in air.

Most peat profiles thus show zonation. There is a relatively shallow surface layer (in Britain usually 5-20 cm, but sometimes more) of rather open structure, containing live and, mostly intact but decaying, dead material. This layer is largely oxygenated, and is referred to as the acrotelm (Ingram 1978). Below this, where the weakened plant material has collapsed, is the waterlogged zone which reaches to the base of the peat. This is known as the catotelm, and

is much more highly decayed, has a higher bulk density and is largely anoxic. The transition from acrotelm to catotelm is not well-defined. There is a zone in which the water table fluctuates and in which, therefore, the degree of oxygenation also changes. The acrotelm contains small anoxic regions, as a result of local waterlogging, for example, and regions of the catotelm may be well-oxygenated, oxygen being supplied from the roots of bog plants such as *Eriophorum angustifolium* (Armstrong 1964). The boundary between the two layers is often taken to be the position of the summer mean minimum water table (Ivanov 1981, cited by Clymo 1984).

Thus a peat bog consists of two physically distinct zones which, largely as a result of the difference in the time over which they have been decaying and in the degree of oxygenation, are also chemically different. In the oxygenated layer mass is lost by leaching, the activity of peat animals such as enchytraeid worms, and through its utilisation as a substrate for microbial respiration. So, accompanying changes in the physical structure and strength of the decaying material are changes in its chemistry, so that when this partially-decayed material is engulfed by the rising water level it provides a different set of substrates for the micro-organisms, or the same substrates in different proportions from those in the original live material. The microbial population responsible for further decay also differs, since it must operate in an anaerobic mode. Collins, D'Sylva & Latter (1978), studying MH peat soils at six sites, found that aerobic and anaerobic bacteria were present and that the aerobic population was greater than that of the anaerobic at all depths measured (≤50 cm), but the relative population sizes changed. Both types decreased with depth though there was a peak in the number of anaerobes in the dark brown (ca. 4-10 cm) and green-brown (ca. 10-19 cm) horizons. The maximum number of facultative anaerobes was found in the green-brown and red-brown (ca. 10-27 cm) horizons.

How is the two-layer system modelled? There is much evidence to indicate a sharp drop in decay rate, sometimes of two or more orders of magnitude, on crossing into the catotelm (e.g. Clymo 1965; Zimenko & Revinskaya 1972; Heal & French 1974; Heal *et al* 1974; Aaby & Tauber 1975; Clymo 1978; Heal, Latter & Howson 1978 and Heal *et al* 1981), so

it is sensible to model the acrotelm and catotelm separately. Both have material added to them at the surface; in the acrotelm this is productivity, in the catotelm it is that material at the bottom of the acrotelm which is incorporated into the catotelm when the water level rises. Both systems reduce this mass input through decay. Thus accumulation in both systems can be modelled using equation (5), employing subscripts to denote a process in the acrotelm (p_a and α_a) or catotelm (p_c and α_c). Acrotelm and catotelm thus each have a theoretical steady-state mass which is reached after a time period dependent on the decay rate in each zone. The accumulated mass in each zone is totalled to give a peat accumulation rate for the whole system.

Numerous estimates of the aerobic decay rate, α_a, exist in the literature, for example, Clymo (1965); Gore & Olson (1967); Heal & French (1974); Heal *et al* (1974); Clymo (1978); Heal, Latter & Howson (1978); Clymo (1983, 1984). They span the range 0.01-0.8 y^{-1}, the value largely depending on the age and type of organic material used and the depth in the surface profile at which the decay was measured. Estimates of the anaerobic decay rate are much less frequent, but all indicate a significant drop in the rate of decay compared to that in the aerobic zone above. For example, Gore & Olson estimate α_c to be 0.001-0.003 y^{-1}; Heal, Latter & Howson (1978) measured weight losses of 29% and 60% for *Juncus* and *Calluna* material, respectively, in the surface zone of a MH peat profile, but only 9% and 18% for similar material at -21 to -25 cm (mean water level was -18.5 cm). At Thursley Common, a wet acidic valley mire in southern England, Clymo (1965) measured the decay rate below the water level of *Sphagnum papillosum* to be 0.01-0.02 y^{-1}, compared with 0.12 y^{-1} at the surface, and in the same set of experiments filter paper (cellulose) decayed at a rate of 0.03 y^{-1} at -75 cm compared with 0.17 y^{-1} in the top 5 cm. Again, in a *Sphagnum magellanicum* lawn (MH) the aerobic decay rate was found to be between 0.03 and 0.06 y^{-1}, depending on the experimental method used, and the anaerobic decay was of the order of 10^{-5} y^{-1} (Clymo 1978). Using profile data of various workers where radiocarbon dates, bulk density and stratigraphy were known Clymo (1983, 1984) estimated the anaerobic decay rate to be between 6.5 x 10^{-5} y^{-1} and

5.5 x 10^{-4} y^{-1}. Accepting, then, that there is a large drop in decay rate when the water table is crossed, it follows that material entering the catotelm remains relatively safe from decay and may persist for a very long time. In contrast, in the acrotelm, up to 80% of the material may be lost before it enters the catotelm. Hence it is the *catotelm* which is the real accumulating system, and the rate at which material is incorporated into it, p_c, and its subsequent rate of decay, α_c, are the most important parameters in the model, affecting the mass of peat which may accumulate. In turn, p_c is dependent on the time material spends in the acrotelm before it reaches the catotelm, which itself is a function of the depth of the acrotelm. Clymo (1983, 1984) calculated the effects on the rate and degree of peat accumulation in the acrotelm and catotelm, and in the total system, according to the model described here in equation (5). (In fact his model was more complex than this, involving two components in each zone which decayed at different rates, but this is an unnecessary complication in the present context, where we are considering integrated values for the entire peat bulk.) Values for p_a, α_a, α_c and the mass of material per unit area in the acrotelm had to be provided for each simulation, and by changing one or more of the parameters it was possible to predict some rather unexpected results. Previously, where indirect estimates of the anaerobic decay rate have been made, the results have been so small that workers have, on the whole, tended to dismiss them as negligible. However, using values of that order of magnitude (x10^{-3} and x10^{-4}) for α_c, the simulation showed that such a low rate was far from negligible. Indeed, it appears that it is precisely *because* the anaerobic decay rate is so low that peat accumulates to the extent it does, and an accurate knowledge of the exact decay rate is vital in predicting the final steady-state mass. For example, if 60 g m^{-2} of dry matter is incorporated into the catotelm each year (p_c) and the anaerobic decay rate (α_c) is 0.0012 y^{-1} then the steady-state mass will be 5.2 x 10^4 g m^{-2}. This is equivalent to 0.52 m, assuming a constant bulk density of 0.1 g cm^{-3}. If α_c were 0.0006 y^{-1}, a change in absolute terms of only 0.0006 y^{-1}, then the potential steady-state depth would be 1.03 m. So it is important to be able to measure very

low rates of decay, and measurements must be sufficiently sensitive and reliable to permit distinction between two very low rates. Secondly, the simulation highlighted the importance of p_c. Given that α_c is 0.0006 y^{-1}, if p_c is 60 g m^{-2} y^{-1}, the steady-state mass of peat accumulated by the catotelm is calculated to be 1.03 x 10^5 g m^{-2}, or 1.03 m if the bulk density is 0.1 g cm^{-3}. If, however, the rate of addition of matter to the catotelm is increased two and a half times, to 150 g m^{-2} y^{-1} (α_c remaining at 0.0006 y^{-1}), the potential depth of anaerobic peat becomes 2.5 m.

The time that plant material remains in the acrotelm, above the water table, greatly affects the rate at which material is subsequently engulfed into the catotelm, since the longer it stays in the zone of relatively high decay rates, the less will remain to be passed on. Time spent in the acrotelm is directly related to acrotelm depth if, as in the proposed model, p_a and α_a are constant (for any one simulation). In the simulation, an increase in acrotelm depth of just 2 cm, from 8 cm to 10 cm, increased the time that plant material spent in the acrotelm by three years (to 10.7 years) and resulted in a 22% drop in p_c. If the depth of the acrotelm was doubled, from 8 cm to 16 cm, time spent in the acrotelm increased from about 8 years to about 31 years, and the rate at which matter entered the catotelm was reduced from 370 g m^{-2} y^{-1} to 70 g m^{-2} y^{-1}.

Other significant effects were demonstrated in further simulation experiments, but the examples quoted should serve to illustrate the importance of the decay rate in the catotelm: despite its small value its effects are not insignificant, and very small absolute differences in its value are capable of producing large effects. The amount of material which enters the catotelm also affects the potential steady-state mass of accumulated peat and this is itself largely determined by the time material exists in the acrotelm before becoming inundated by the rising water level. For a given aerobic decay rate, less material will survive to enter the catotelm the deeper the acrotelm.

To return briefly to the question which introduced this consideration of a two-layer system, the reason for the discrepancy between the steady-state depth predicted from a single-layer model and the known depth of peat bogs should now be apparent. The one-layer

system model, with the values used ($100 \leq p \leq 200$ g m^{-2} y^{-1}, $0.01 \leq \alpha \leq 0.1$ y^{-1}, $\rho = 0.05$ g cm^{-3}, all realistic values for the acrotelm), predicts reasonable steady-state depths for *that* system.

In the absence of measurements of α_e, attempts have been made to estimate its value indirectly from models of peat growth. Clymo (1984) has reformulated equation (6) to give an expression relating the depth of peat *below* any chosen datum to its age relative to that datum. The resultant equation is formally the same as equation (6), above, but zero time may be *chosen*; it is not necessarily equated with the initiation of peat formation. In effect, time runs *backwards* from that point:

$$V = \frac{p}{\alpha}(1-e^{-\alpha T}) \qquad (10)$$

V is the depth, measured in units of mass, below the chosen datum, and T is the age of the peat relative to the same point. From this equation it is possible to calculate the expected value of α for any portion of the peat profile for which at least three mass-depths and their corresponding ages are available. Solving the three equations simultaneously eliminates p/α, and leaves α calculable in terms of V and T. In practice, however, there are problems and disadvantages with this method of estimating α. Although there are numerous radiocarbon- and pollen-dated profiles reported in the literature, they nearly all use linear depth; the bulk density is not recorded and so the mass-depth is not known. It is possible to proceed by assuming bulk density, ρ, is constant, but where profiles of ρ are published, this is clearly not the case (e.g. Pakarinen & Tolonen 1977; Tolonen 1977; Jones & Gore 1978; Clymo 1983, Fig. 4.18 and this study). A second objection to the method is that, as described, it relies on just three points in the profile. Better, would be to fit equation (10) to a larger data set, extending over as much of the profile as possible, by a minimisation technique. Clymo (1984) found five cases, all Scandinavian, where corresponding age and mass-depth profiles were recorded (Nilsson 1964 (bulk density values not published); Tolonen 1966, 1977 (two profiles) 1979; Donner *et al* 1978), and applied such a

minimisation technique to them. Inherent in such a method is a test of the model being used; here, specifically, an evaluation of the assumption that α (and p) is constant, and that it is exponential. The five Scandinavian profiles were between 5 m and about 7 m deep, and yielded estimates of α_c of between 6.5 x 10^{-5} and 5.5 x 10^{-4} y^{-1}. The anaerobic 'productivity', p_c, was estimated at between 3.6 x 10^{-3} and 7.8 x 10^{-3} g cm^{-2} y^{-1}. A sixth profile, also from Scandinavia (Aaby & Tauber 1975), provided very detailed age data (55 points over 2.5 m), and although bulk density had not been recorded it was possible to derive (Clymo 1983) the information from the von Post humification scale (von Post & Granlund 1926), which was. The resultant values of α_c and p_c were 1.4 x 10^{-5} y^{-1} and 53 g m^{-2} y^{-1}, respectively. Earlier (1978), Clymo had elaborated the model presently under discussion to include the effects of consolidation. It predicted anaerobic decay rates of between 10^{-12} and 10 y^{-1}, but with most estimates lying between 10^{-6} and 10^{-2} y^{-1}. (In the same paper Clymo estimates α_c from methane efflux at the surface of the study bog (Burnt Hill at MH) to be 10^{-5} y^{-1}. He assumed that all methane derived from the catotelm and that none was oxidised before it reached the surface.)

The relationship between mass-depth and age would be linear if there were no decay but, though less so than for linear depth versus age, such a curve *is* concave. It is the non-zero value of α_c which is responsible, and which prevents the peat accumulating indefinitely: instead, it moves towards a steady-state mass.

1.3 AIMS AND CHOICE OF METHODS

The primary aim of the present study was to obtain measurements of the anaerobic decay rate in ombrogenous peat, since these have hitherto been lacking in the literature and are necessary for further testing of current peat accumulation models, in particular those which have been based on the arguments set out above.

The methods commonly used to measure (aerobic) decay cannot be employed here. The 'litter bag' technique in which material is buried in nylon mesh bags and weighed at intervals to determine the time-course of mass lost is not sufficiently sensitive to detect changes in

mass of, say, 1.0×10^{-4} g and 2.0×10^{-4} g. This would be necessary in order to distinguish between a decay rate of 0.001% and 0.002% in one season, using a litter bag originally containing 10 g dry weight of material, which is the amount commonly used per sample. Loss of one tiny fragment of material from the mesh, through disturbance or through removal by soil animals, would be enough to invalidate the results obtained. Similar arguments of insensitivity and inaccuracy apply to the burial of standard materials in order to follow their weight loss. The problems of physical disturbance during sample removal would be compounded when working deep in the peat.

Another way to measure decay is to measure the products. In the present context the main ones are methane (CH_4) and carbon dioxide (CO_2). Such methods have been adopted on numerous occasions to measure the flux, particularly of CO_2, at the surface of mineral soils (e.g. Douglas & Tedrow 1959; Witkamp 1969; Edwards & Sollins 1973; Baldocchi *et al* 1986), and that of CH_4, CO_2, or both, above bogs and tundra sites (Douglas & Tedrow 1959; Clymo & Reddaway 1971; Peterson & Billings 1975; Svensson 1976, 1980; Harriss, Sebacher & Day 1982; Harriss *et al* 1985; Svensson & Rosswall 1984; Yarrington & Wynn-Williams 1985). The resolution of the gas chromatographic (or infra-red gas analysis) techniques which are used to quantify the gas samples presents no practical limitation since it is possible to distinguish between two sample concentrations at orders of magnitude down to about 10^{-11} mol cm^{-3} (1 ppm). This contrasts with the reasonable limits of about 10^{-4} mole for measurements of material dry weight. In both cases the largest errors will arise from sample collection and manipulation prior to measurement. In the present study such errors have been minimised by avoiding the need to disturb the peat profile after the initial installation of the samplers, and by standardisation of the collection, storage and analytical procedures. They have the further advantage of providing both quantitative and qualitative results simultaneously, in contrast to litter bag and standard material techniques.

To complement the gas measurements, data were collected for selected characteristics of the peat profile to provide general environmental

the profile from which the gas samples were collected. To this end stratigraphy, air and peat temperatures, pH, redox potential, total sulphide concentration, depth of the water level and the position of the 'sulphide zone' (Urquhart 1966; Urquhart & Gore 1973) were recorded. Changes in each with depth and season were followed, from which data it was hoped to highlight the factors most important in determining (limiting) the activity of the micro-organisms, and hence decay. The relative importance of such environmental factors may not be consistent at all depths, and it may be erroneous to assume that results obtained from the surface, oxygenated zone, can be applied directly to the deeper regions of the catotelm.

The work falls into three, not always distinct, parts. For convenience and not in any order of priority, these are

i) laboratory work

ii) garden work

iii) fieldwork.

The description of the Materials and Methods used (Chapter 3) is set out according to this general framework. Results (Chapter 4) are reported collectively, as a series of topics under investigation. Finally, the Discussion (Chapters 5 and 6) follows a more integrated approach, dealing firstly with the quantitative results, and secondly with the qualitative, environmental factors.

CHAPTER 2

FIELD SITE DESCRIPTIONS

No glory or pomp lights Snuggedy Swamp
Down by the Barrier Bay,
For life's really harsh
In this duckety marsh
Where the microbes are working away

Origin unknown

FIELD SITE DESCRIPTIONS

2.1 INTRODUCTION

Two Sites were used for fieldwork; Moor House National Nature Reserve (MH) and Coom Rigg Moss National Nature Reserve (CR). Both are situated in the Northern Pennines and have similar peat composition. The same programme of monitoring and sampling was carried out at each Site, for comparison.

2.2 MOOR HOUSE NATIONAL NATURE RESERVE

A map of MH is shown in Fig 2.1. A subjective classification of the area, based on temperature curves (French 1974) described it as having a warm, oceanic climate. A detailed description of the Reserve, including soils, vegetation and climate, is given by Heal & Smith (1978). This, and Smith (undated) have been used for the following general account.

The Reserve covers an area of moorland roughly 4000 ha in extent, between about 300 m and 845 m altitude, at latitude 54°N, longitude 2°W. It straddles the Pennine ridge. The present study used only the part of it known as Burnt Hill (GR NY754328), an area of blanket bog on the boulder clay overlying Carboniferous limestone to a depth of 2.5-3.5 m. The general topography of this area is a plateau, very gradually sloping down towards the east. The surface of Burnt Hill shows a well developed hummock-pool topography, bounded by eroding peat laggs and stream banks. Fieldwork was carried out on the hummock-pool area; Fig. 2.2 shows the results of a plane-table survey of the complex. Numbers indicate the sampling sites. The vegetation on Burnt Hill covers a spectrum of species and associations from those of the (relatively) dry hummocks, situated several centimetres above the water table, to those constituting the *Sphagnum* lawns, and finally the pool species. The general blanket bog cover is Calluneto-Eriophoretum (McVean & Ratcliffe 1962), but in the wetter patches *Calluna* and *Eriophorum vaginatum* decrease and *Scirpus caespitosus* becomes more frequent, thus approaching their Trichophoro-

FIELD SITE DESCRIPTIONS

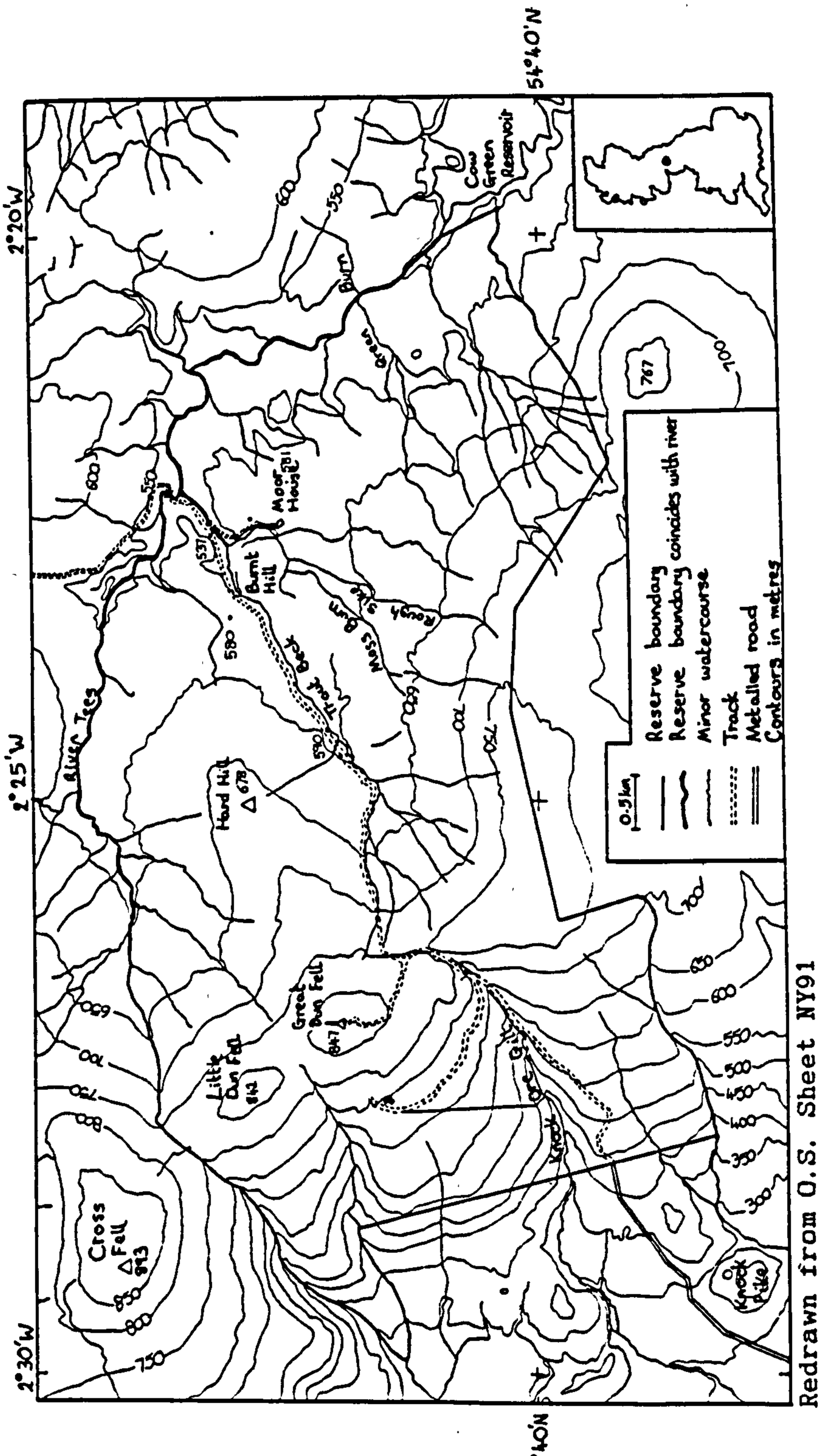
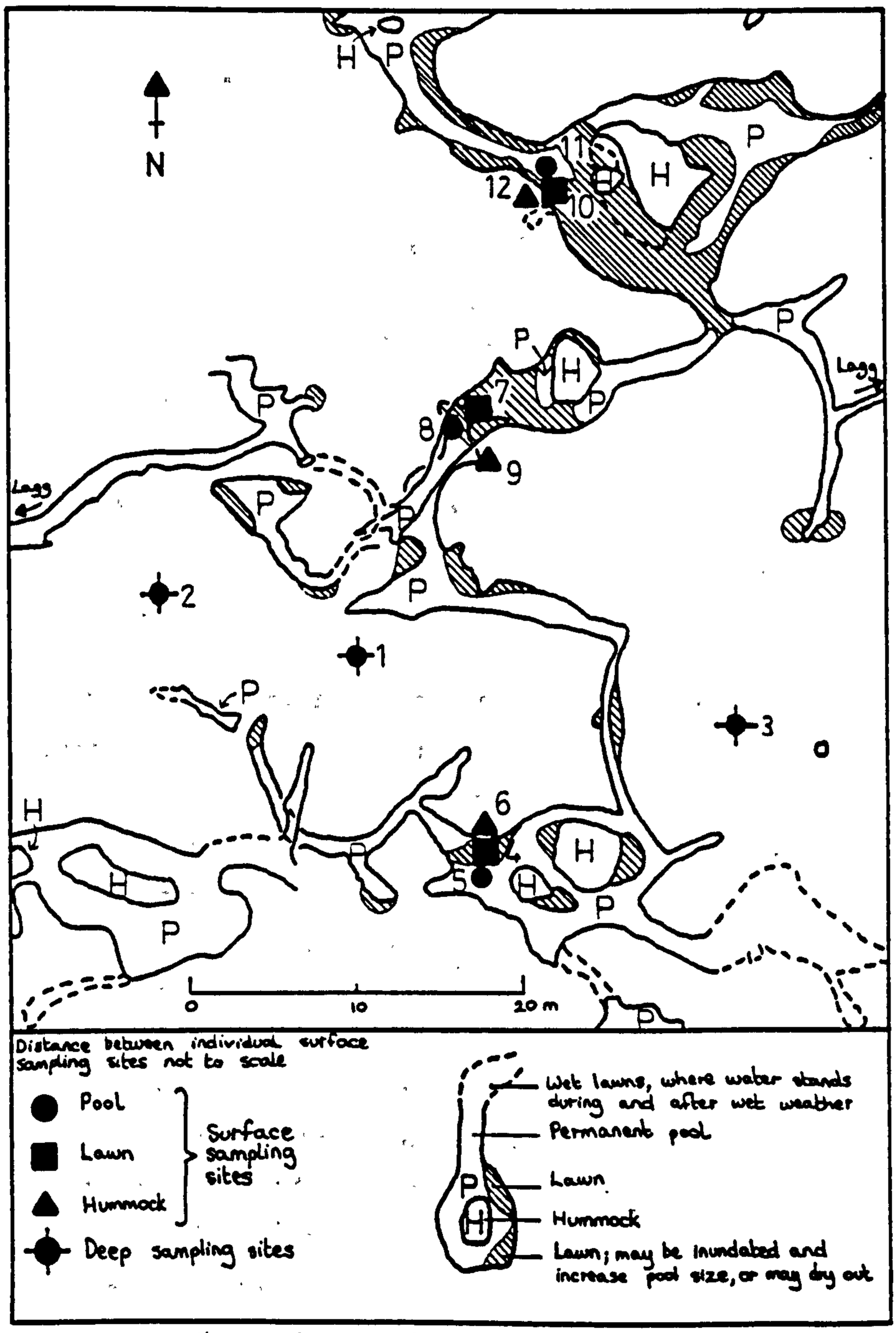


FIG. 2.1 Moor House National Nature Reserve

Redrawn from O.S. Sheet NY91

Eriophoretum. The species commonly found in each of the pool, lawn and hummock microhabitats are given in Table 2.1. Appendix A lists

FIG. 2.2 Area of Burnt Hill pool-hummock complex used for sampling



the most important species comprising the surface vegetation at each of the sampling sites.

Burnt Hill lies at an altitude of 575 m and is exposed, hence the weather conditions can be severe. August is usually the warmest month; the ten-year mean temperature (½(max. + min.)) for 1961-70 was 10.7°C. For the same period the mean August highest maximum was

TABLE 2.1 Typical species found on Burnt Hill hummock-pool complex.

	Vascular spp.	*Sphagnum* spp.	Other bryophyte spp.
Pool	*Eriophorum angustifolium*	*S. cuspidatum*	
Lawn	*Eriophorum angustifolium*	*S. papillosum* *S. subnitens* *S. capillifolium* *S. imbricatum*	
Hummock	*Calluna vulgaris* *Eriophorum angustifolium* *Eriophorum vaginatum* *Erica cinerea* *Scirpus caespitosus*	*S. capillifolium* *S. papillosum* *S. magellanicum*	*Dicranum scoparium* *Odontoschisma sphagni*

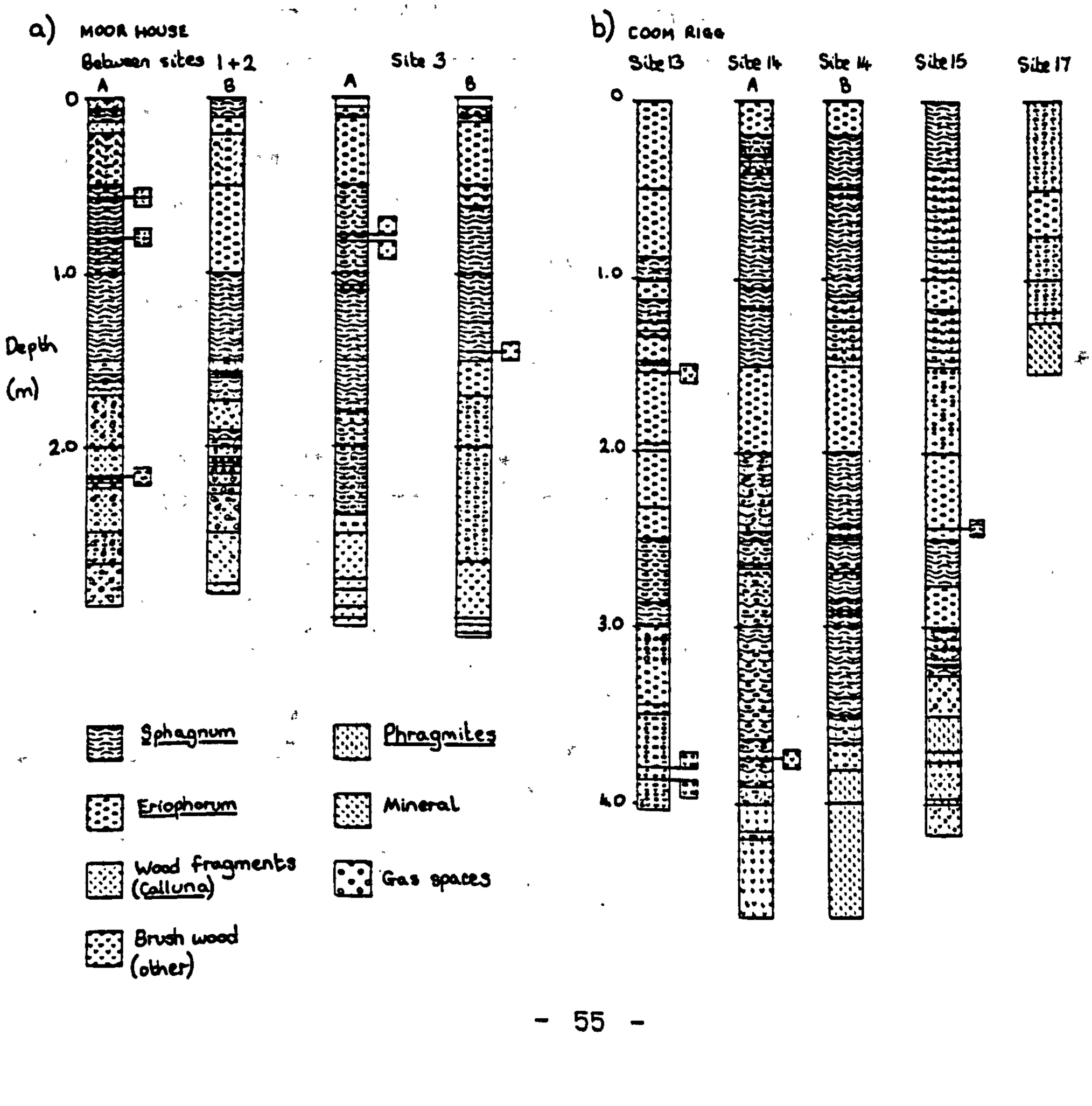
20.3°C. December, January and February each gave a mean temperature below 0°C in 1961-70, the lowest mean absolute minimum occurred in February (-11.8 °C), and the extreme low was -18.3 °C, also in February. These figures all refer to the meteorological station adjacent to Moor House (the building) at an altitude of 558 m (GR NY758328). This is 17 m lower than the Burnt Hill plateau. Heal & Smith (1978) report a drop in mean annual air temperature of about 0.53 °C for an increase in altitude of 100 m, thus the expected difference between the meteorological station mean temperatures and those of the study area is probably negligible. Frost may occur in any month, and snow usually lies from October to May. Annual rainfall is about 2000 mm, spread unevenly over the year. Based on the ten-year mean figures, June is the driest month (mean rainfall 114 mm), but this obscures the variation; individual year records show that the driest month may occur at any time between April and August. Like the summers, the winters are often cloudy, and winds may exceed 87 knots (≡ 100 mph) on occasions, though the ten-year annual mean was about

14 knots, with a drop of roughly 2-3 knots in the summer compared to the winter. •

So, the summers are cool and wet compared with the national average (though as was noted above, the MH climate was classified as warm and wet in relation to the other IBP tundra biome sites), and the winters cloudy and wet. The climate allows only a short growing season (taken as days with mean temperature above 5.6 °C) of about six months, from May to October.

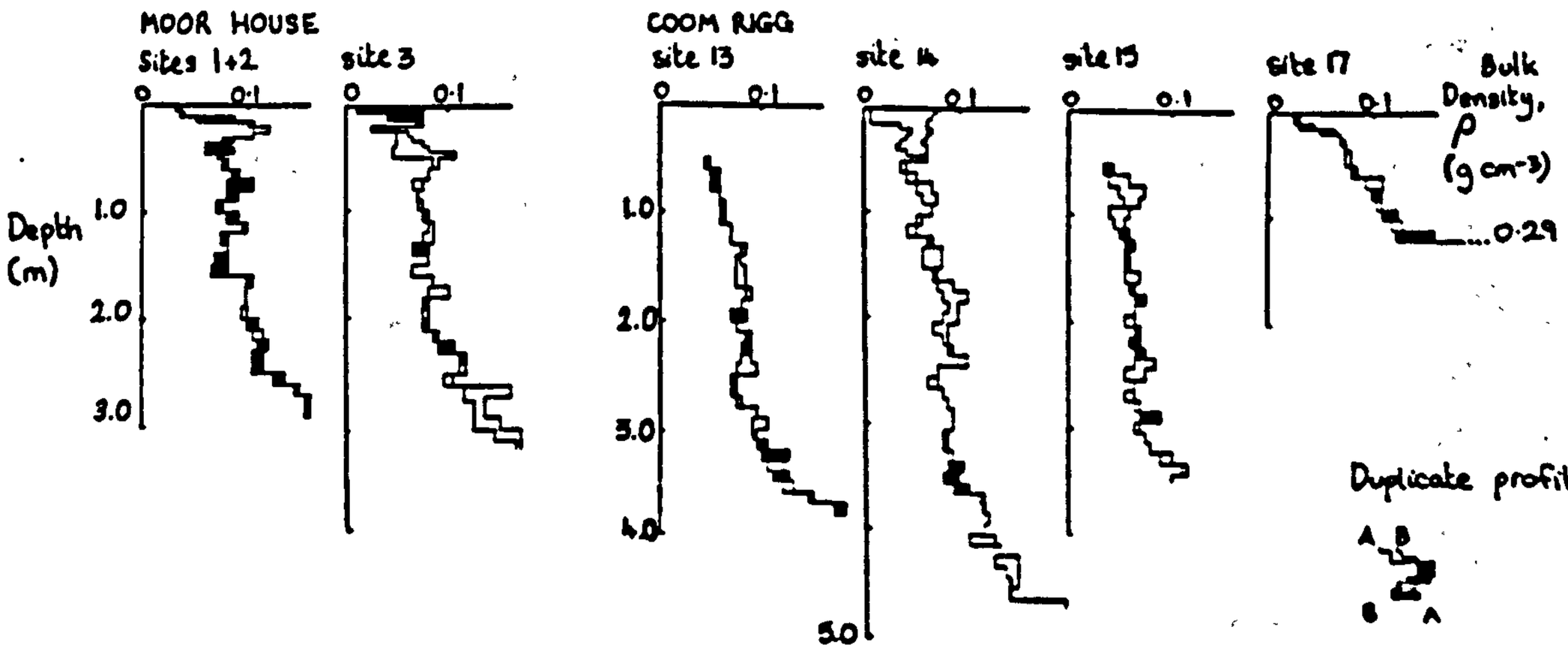
Sphagnum and *Eriophorum* are the main species forming the peat (Fig. 2.3a), which is about 3 m deep at the sampling sites. There is considerable variation in the composition and structure of the peat both within and between profiles at all scales. Commonly, differences within the surface layers (top 30 cm, say) are more highly contrasting, but it has proved possible, indeed constructive, to recognise certain recurring general features and to incorporate these

FIG. 2.3 Stratigraphy of Moor House and Coom Rigg sampling sites



into peat profile descriptions in the form of horizons, as for mineral soils. Thus, keeping in mind that local conditions will modify any general pattern, it is possible to divide the surface profile into a litter layer, in which freshly-dead, intact material exists in very little-altered form, with an underlying dark-brown or black horizon in which the plant material is still physically intact, but is chemically somewhat changed and has lost its green colour. Below this is a green-brown or green horizon in which the material is lower in 'nutrients' such as K, Na and Mg (Brown & Veum 1974), and which darkens on exposure to air. The deepest of the horizons is the red-brown or red horizon, in which the original material is considerably humified and in which reducing conditions prevail. Precise depths for each of the horizons vary. The degree of humification continues to increase down the peat profile, the fibre content decreases, and *Sphagnum* plants (and others) become increasingly fragmented. On Burnt Hill the peat towards the base of the profile is of a buttery consistency, though some *Sphagnum* leaves and *Eriophorum* leaf epidermis are still recognisable. At the very bottom there is evidence of other vascular plants and very small woody fragments. These were not identified, but are likely to be birch, which is common at the peat base in other parts of the Reserve. Details of the stratigraphy and

FIG. 2.4 Bulk density profiles for Moor House and Coom Rigg sampling sites



bulk density at the sites used for gas sampling at MH are included in Figs. 2.3 and 2.4, respectively.

The pH of blanket peat is very low; usually about pH 3.0-4.0, with limited variation down the profile. In contrast, the redox potential changes considerably as the profile is traversed, initially declining to a minimum, commonly in the green-brown horizon. There is much variation in the pattern of change below this minimum, but in general the redox potential in the peat is low, and conditions soon become reducing below the surface. This is a direct result of the high water table, characteristic of blanket peat, which at Burnt Hill was between about 5 cm and 10 cm below the general bog surface at most times of the year, though of course there was large local variation relative to the actual surface because of the small-scale topography.

Further details of pH and redox potential profiles and of water table changes and peat and air temperatures are given in Chapter 4, together with sulphide concentration profiles.

The MH sites were used to measure changes in gas production with depth and season, over a roughly constant total peat depth, and the effect of microhabitat on the flux of peat gases from the surface.

2.3 COOM RIGG MOSS NATIONAL NATURE RESERVE

Coom Rigg Moss NNR was used as the second field site. It is an area of bog about 40 ha in extent, situated amongst the Forestry Commission plantations of the Kielder Forest, in Northumberland. Its position (GR NY6979) is shown in Fig. 2.5. Numbers refer to the sampling sites.

The stratigraphy and vegetation, chemistry and hydrology are described in a series of papers by Chapman (1964a, 1964b, 1965).

Coom Rigg Moss lies at an altitude of about 325 m, that is, almost 250 m lower than MH. Continuous climatic measurements are not available for the Reserve. Temperatures measured during the present study are given in Section 4.1.2 and Appendix G. In general, though,

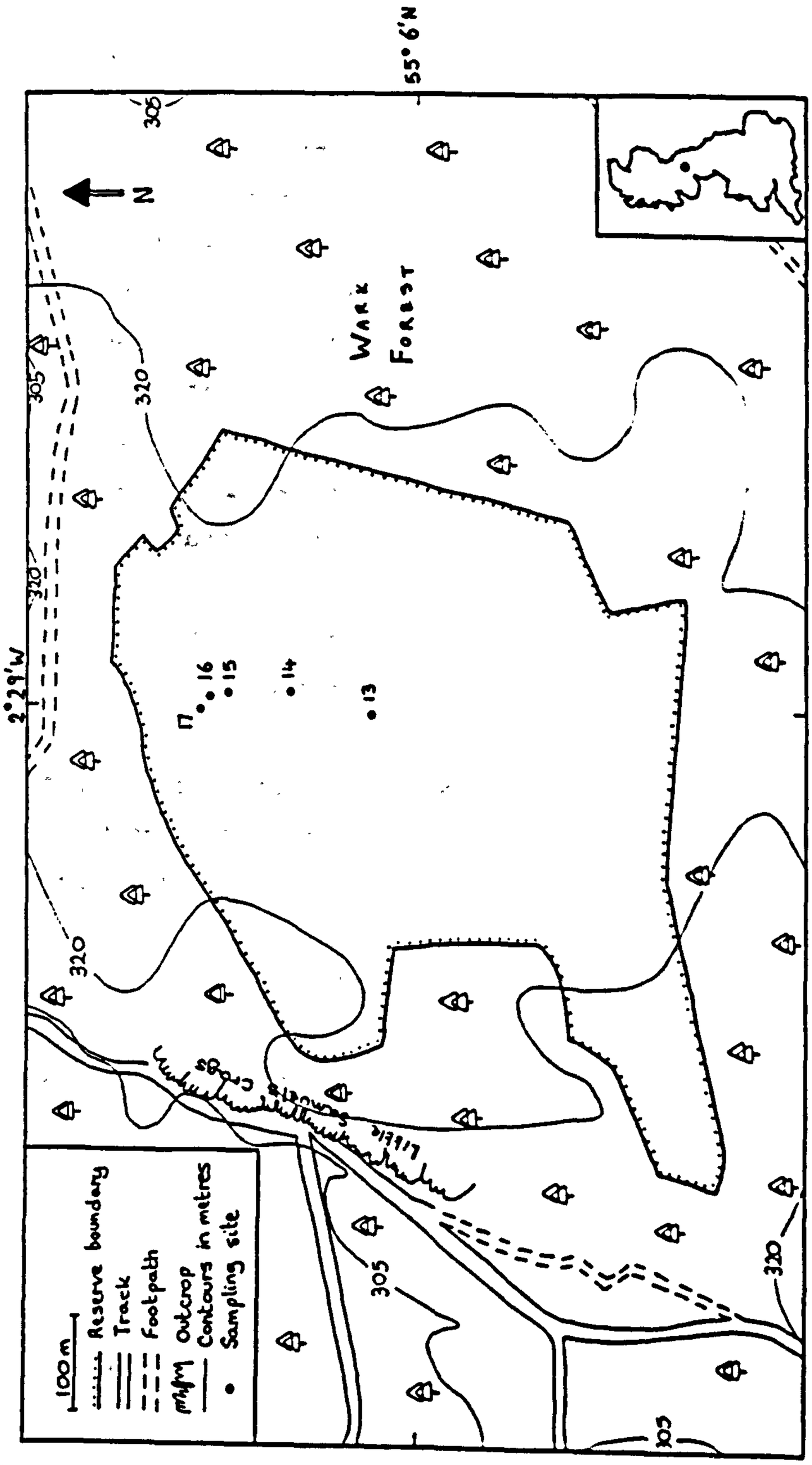


FIG. 2.5 Coom Rigg Moss National Nature Reserve

the climate is similar to that at MH in that the summers are cool and wet, the winters are severe by British standards, and there is a relatively small annual temperature range. Although at a lower altitude, temperatures recorded at CR were occasionally significantly cooler than for the corresponding period at MH. Chapman (1964a) reports an annual rainfall of about 1270 mm.

The relatively flat surface of CR obscures the more complex basal topography; the solid geology is similar to that at MH, with interbedded shale, sandstone and limestone, covered with impermeable glacial boulder clay. A central ridge runs north-south under the Moss with a second ridge running northwest from this. Between the ridges are shallow 'valleys', and in addition there are small-scale, more circular, depressions. From stratigraphical studies (Chapman 1964a) and chemical profiles (Chapman 1964b) it appears that there are two main types of peat profile on the Reserve. In the hollows the accumulated peat records a hydroseral development, from *Phragmites* fen peat, through alder (*Alnus*) and birch (*Betula*) carr to the *Sphagnum-Eriophorum* peat which occurs in the uppermost parts of the profile. Thus the hollows, which are generally 2 to 6 m deep but may be up to 8 m, show a raised bog profile. Their surfaces have now coalesced with the shallow *Sphagnum-Eriophorum* blanket bog peat covering the remainder of the Reserve to a depth of about 1 or 2 m. This blanket peat formed directly on the glacial drift as an ombrotrophic peat. Consequently, the surface now displays a generally uniform topography and surface vegetation, but there is some variation which results from the basal topography and the hydrology (Chapman 1964a, 1965). The extreme example is on the eastern side of the Reserve where relict *Phragmites* still grows. However, most of CR, including the areas used for sampling in the present study, display a typical assemblage of upland blanket bog species. *Sphagnum* mosses form a continous carpet in which liverworts and vascular plants grow. These include the cranberry, *Vaccinium oxycoccos*, but not cloudberry, *Rubus chamaemorus*, which was found on Burnt Hill. The water level is constantly high, usually within 6-10 cm of the surface; standing water does not normally occur in the areas used for this study. Although the general surface is flat, there are undulations, and the plant

associations of an area reflect the water régime (and chemistry, Chapman 1965). *Calluna*, *Eriophorum vaginatum*, *E. angustifolium*, *Scirpus caespitosus*, *Drosera rotundifolia* and *Narthecium ossifragum* are all common at sites 13-16, their relative abundance varying slightly with the conditions. The lagg at the northern edge of the bog, in which site 17 was located, is about 5-10 m wide. The vegetation there is dominated by *Molinia caerulea*, *Polytrichum commune* and *Sphagna*. Being immediately adjacent to the conifers this area probably has a different nutrient status (and drainage) from the remainder of the areas sampled. Details of the species on each sampling site are given in Appendix A.

The hydrology of CR is fairly complex because of the small-scale changes in basal topography (Chapman 1964a, 1965), but the sampling sites used for the present study were all located on the eastern slope of the north-south ridge, and hence any flow presumably is eastwards. They were positioned over a range of total peat depths from about the centre of the bog to the lagg on the northern boundary, adjacent to the Forestry Commission plantation margin.

The general trends in the chemistry of the peat down the profile which were described for MH, above, also apply to CR, but there are clear changes in the chemistry of the deep profiles at CR which reflect the transition from minerotrophic to ombrotrophic development (Chapman 1964b).

As at MH, profiles of the composition and bulk density of the peat at the sampling sites were investigated. These are included above in Figs. 2.3 and 2.4, respectively. (It was not possible to core at site 16 because of matted surface and sub-surface vegetation.) As was explained above, the deeper peat deposits contain towards the bottom remains of *Phragmites* and woody species not found in such variety or quantity at MH. However, the majority of the peat profile is made up of *Sphagnum-Eriophorum* peat, as at MH.

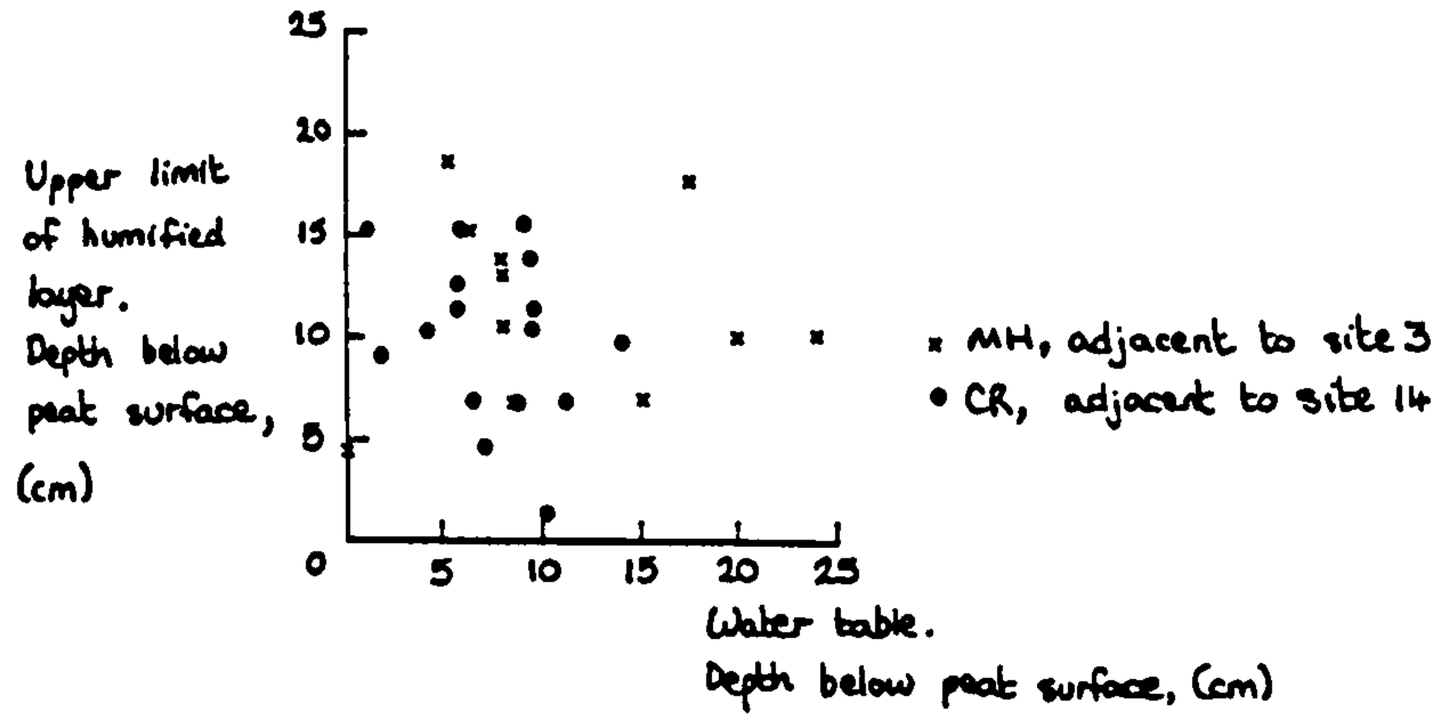
Details of pH, redox potential, sulphide concentration and peat temperature are given in Chapter 4.

The CR sites were used to compare surface gas fluxes over different total depths of peat, and to investigate peat gases from deeper down than was possible at MH.

2.4 LOCAL VARIATION IN PEAT CHARACTERISTICS

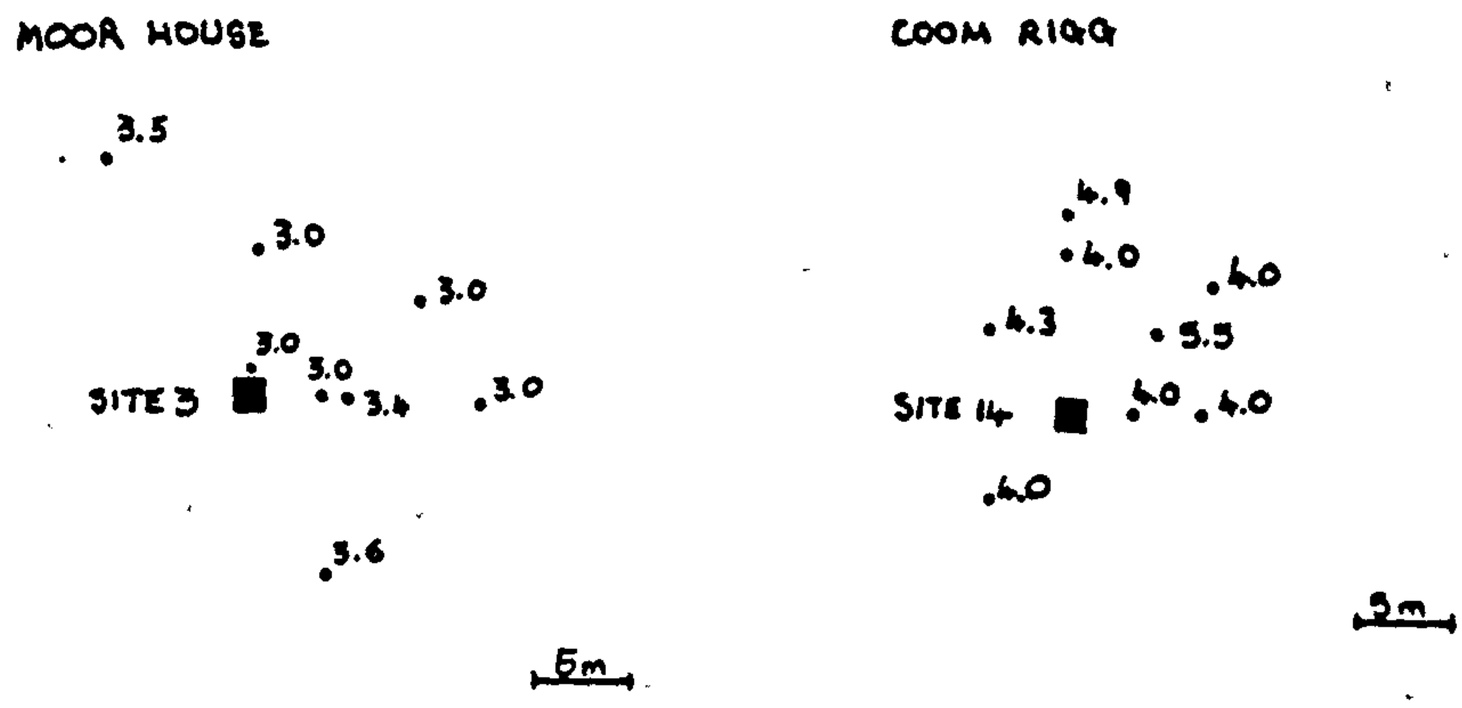
The previous two sections gave general descriptions of the MH and CR field study Sites. In addition to this, repeated coring of restricted areas at both Sites for measurement of pH, redox potential and sulphide concentration profiles (Chapter 4.4) allowed some assessment of the local variation in total peat depth, water level and the upper limit of the humified layer (acrotelm/catotelm boundary).

FIG. 2.6 Local variation in depth of water table and upper limit of the humified layer



Inspection of the field notes revealed variation in all three, and water level and humified layer depths varied in both absolute and relative terms (Figs. 2.6 and 2.7). The differences occurred over very short horizontal distances, sometimes over as little as 6 cm. The range in the total depth of peat measured at eight sites within a radius of 15 m of site 3 at MH was 3.0 m to 3.6 m, compared to a range of 4.0 m to 5.5 m in a similar radius of site 14 at CR.

FIG. 2.7 Local variation in total peat depth



CHAPTER 3

MATERIALS & METHODS

Oh the anaerobes romp in Snuggedy Swamp,
The lignins and waxes decay
And down a few feet
They have turned into peat
(Or even - ahem - into THDM*)
Just as the researchers say.

* Translucent humic degradation matter.

Origin unknown

MATERIALS AND METHODS

3.1 LABORATORY WORK

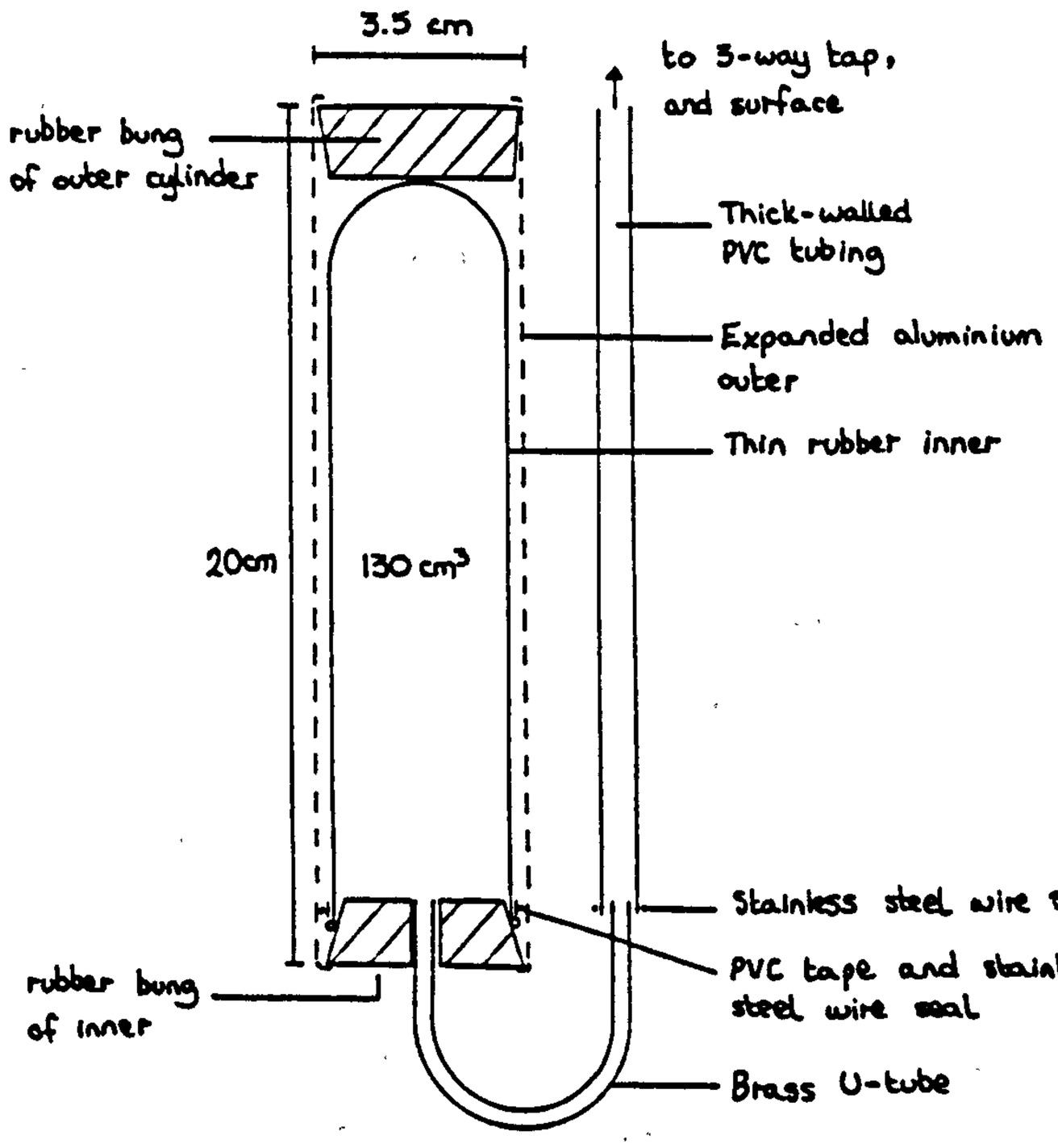
3.1.1 GAS SAMPLERS

GAS SAMPLER DESIGN

The gas samplers used for the collection of both surface and deep peat gas samples were of the same design. The rationale behind the design is given in the next section (Properties of Samplers), specifications of parts can be found in Appendix B. The present section is purely descriptive.

A gas sampler (Fig. 3.1) consisted of a thin rubber inner of standard thickness (0.05 mm) plugged at its open end with a rubber bung. One end of a U-shaped brass tube was passed just through the centre of the rubber bung and then retracted very slightly to prevent

FIG. 3.1 Gas sampler design



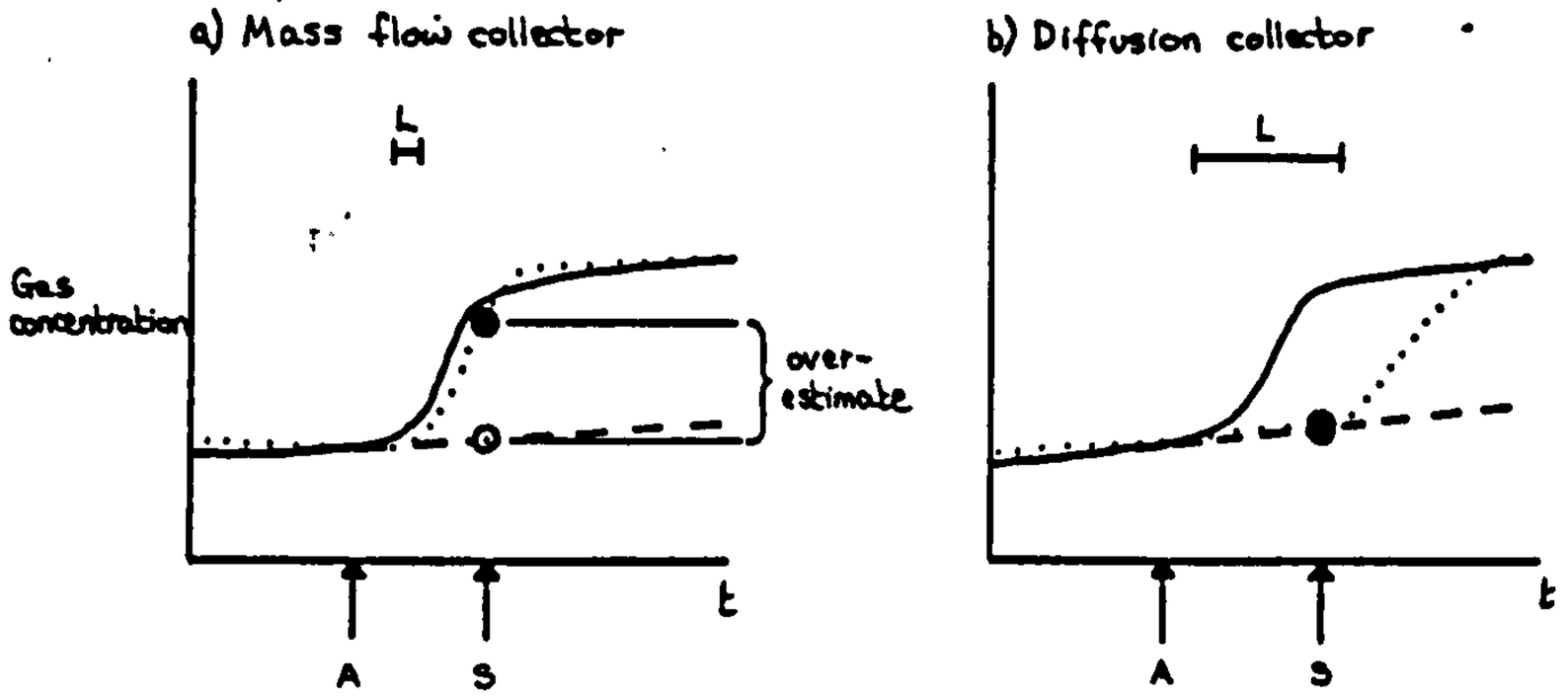
it snagging the inner during inflation or sampling, care being taken to ensure the fit was water-tight. The necessary length of small-bore, thick-walled (I.D. 2.0 mm, O.D. 4.0 mm) PVC tubing was then determined for each sampler and this was wired on to the other end of the brass tubing and then sealed at the far end by a 3-way nylon medical tap. The sampler inners were protected from physical damage by an expanded aluminium cylinder of fractionally larger diameter than the inner and held in place by crimping the open ends of the cylinder around a rubber bung at each end. The rubber bung of the inner was used at one end, a second bung was used at the other. The enclosed volume of the sampler was 130 cm^3. Samplers to be used for the collection of surface peat gases were fitted with 20 cm of PVC tubing, those for deep peat gas samples with sufficient length to reach the surface of the bog from the sampling position, plus 20 cm to facilitate manipulation at sampling time.

PROPERTIES OF SAMPLERS

Samplers were designed to have the following properties.

i) Gas-permeable gas collector; permeable in both directions to any likely peat gases, and to N_2, and at a rate which would make the sampling period (> equilibration period, see below) practicable. The need for a gas-permeable device which collected a peat gas sample as a result of gas diffusion rather than mass flow arose in order to solve the problem of taking samples from deep peat where the gas would be under pressure, and might be present in bubbles. Further, any such bubbles close to the surface might be released under excessive pressure, such as that exerted on approach for sampling. This is often evident when pools are approached; bubbles are seen to rise to the surface as far as a metre ahead. Hence it was necessary to avoid including such erratic gas concentrations in samples, and the time lag inherent in a diffusion-based system of collection ensured that, if samples were collected immediately a sampler was approached, the increase in ambient gas concentration was not included (Fig. 3.2). The final design of gas samplers incorporated a thin (0.05 mm) rubber

FIG. 3.2 Comparison of gas collection by mass flow and diffusion methods



—— ambient gas concentration

.... gas concentration inside collector, including disturbance effect

– – Concentration at which collector and ambient gases are in equilibrium, without disturbance (by extrapolation from rate of concentration increase prior to approach).

● gas concentration inside collector at sampling, after initial equilibration, but following disturbance.

○ as ●, but without disturbance

A approach (disturbance)

S time at which sample taken

L time lag between take-off point of concentration increase in ambient gases and that inside gas collector, following disturbance.

inner which was permeable to gases in both directions over its entire surface. The cylindrical shape of the inner afforded a favourable surface area : volume ratio which reduced the time required for the concentration of gases inside and outside the sampler to reach an equilibrium.

ii) Water-tight gas collector; to allow direct injection of 'dry' gas samples (i.e. containing no liquid water) into the gas chromatograph and thereby avoiding poor reproducibility of component responses (trailing peaks and inconsistent retention times caused by excessive water on the columns) or the need for head-space manipulations. Of course, water vapour will inevitably be present in all samples. By using a rubber bung to plug the open end of the inner, and by cushioning the delicate membrane with PVC tape, the seal between the rubber inner and bung was made water-tight by a length of stainless steel wire wrapped around the two and drawn up tight by twisting until it could be seen biting into the tape and rubber layers beneath.

iii) Sufficiently strong to withstand a considerable amount of physical battering. In the case of the deep peat gas samplers, these would have to be forced down into the peat to whatever depth they were required, without sustaining any damage. Surface gas samplers were to be transported back and forth between the laboratory (London) and the field sites many times over the duration of the study in addition to their being handled at the field sites. Each of the thin rubber inners was therefore fitted with a protective cylinder of expanded aluminium, as described above. The cylinder was very slightly larger than that of the inner and was fully permeable to gases (and water).

iv) Able to be sampled and refilled repeatedly without disturbance or damage to the sampler itself or to the surrounding peat for at least the three-year duration of the study. This posed no problems when considering the design of the surface samplers, since these would be readily accessible, and the method of surface gas collection envisaged (next section) was non-destructive with respect to both peat and sampler. For deep peat gas collection the basic sampler design had to be modified so that each sampler could be buried in the peat at the required depth on the first visit, and subsequently all sampling could be carried out from the surface without disturbance. This was accomplished simply by attaching to the brass U-tube a sufficient length of thick-walled, narrow-bore PVC tubing to reach back up to the surface, plus about 20 cm for manipulation.

It is known that gases are able to diffuse through PVC of the type used for the sampler tubing, but the rate of diffusion from the surrounding peat was not determined. However, the longest piece of tubing used was 5 m, having a volume of 35.5 cm^3, or 27% that of the sampler inner (130 cm^3). This may appear a significant volume to act as a source of contamination to the collected gas below, but, because of i) the thickness of the PVC tubing wall, ii) the very small area for downward diffusion, and iii) the concentration gradient for diffusion, this is not so. Thus even the maximum length of tubing used cannot act as a significant source of contamination of the desired sample from gases higher up the peat profile.

v) Properties i)-iv) must hold under pressures greater than atmospheric (i.e. >101 kPa). This, because the same basic sampler

design incorporating the same materials and operating in the same way was to be used for samplers buried deep in the peat as well as for those on the surface. A column of water 10 m high delivers a pressure at its base of +101 kPa (≃ $1x10^5$ N m^{-2} ≃ 1 atm ≃ 1 bar ≃ 760 mm Hg). If we argue that, as a first approximation, peat acts like a column of water, the pressure delivered at a point 5 m down the peat profile (the position of the deepest sampler) will be approximately 150 kPa, and this is thus the maximum pressure under which a sampler must operate. Tests were carried out to see if it was feasible to inflate a sampler under pressure. Results showed that it could be repeatedly inflated and deflated, and that it remained water-tight. Properties i)-iv) were tested under increased pressure in samplers in the laboratory and in field trials. Samplers were fully operational down to the required depth in the peat.

vi) Must be of simple design, made from inexpensive, readily-available materials, and easy to assemble with the facilities available at the university. This, because a large number of samplers would be needed and may have to be replaced, after damage, at short notice.

Testing the sampler design is described in Appendix C.

OPERATION OF GAS SAMPLERS

a) Principle

Both surface and deep peat gas samplers worked on the same principle. Each was filled with either N_2 or air until just inflated, sealed, and left in position for as long as necessary for an equilibrium to be set up, by diffusion, between the gases in the sampler and those in the surrounding atmosphere (surface samplers) or peat (deep samplers). Once the equilibrium had been reached a sample was withdrawn, which thus represented the gases present around the sampler. Thus, once in position, both the surface and deep peat gas samplers collected gas in the same way, but there were differences in the manipulation of the samplers and in the information derived from the samples they collected. Data from the deep peat gas samples gave a measure of the *concentration* of gases present at that depth,

assuming that the concentration does not change significantly over the sampling period. In contrast to this, the surface sampler data provided a measure of the *flux*, that is, the *rate* at which gases were being evolved from the surface of the bog. The diffusion of gases in water is much slower than in air (by about x 10^{-4}). so gases dissolved in the peat water around the sampler will be less mobile than gases present in the shallower, non-waterlogged peat above. Furthermore, mass flow occurs to a significant extent in the shallower peat: in run-off water and with air currents. Neither of these factors has a significant effect on the transport of gases through the waterlogged regions (Ingram 1983). This leads to the assumption that, given a constant, very slow, rate of production, the deep peat gas concentrations are effectively stable, and a sampler buried in the peat will come to contain a gas sample which will reflect reliably the ambient concentration of components. On the surface, however, conditions are much less stable and any gas evolved, even in relatively large quantities, is likely to be quickly carried away in air currents, or to be significantly diluted. The concentrations of gases evolved from the surface may thus be modified drastically and, worse, unpredictably. The additional problem of erratic, unnatural, releases of gas from the surface of the sampling area has already been discussed above (Properties of Samplers). In order to standardise the sampling and to obtain meaningful results, the field surface gas samplers were enclosed in a sealed bottomless bucket which was sunk into the peat to a depth of 20 cm at each of the surface sampling sites. The buckets were made of heavy duty polythene, with a diameter of 32 cm and a total height of 40 cm. The bottom was cut out of each bucket to give a cylinder which, once positioned in the peat at the beginning of the study, was left in place throughout and was used to mark the exact sampling areas. Surface gas samplers were put out into the buckets for two days on each visit to the field and taken away at the end. Having ensured their sampling consistency experimentally in the laboratory, samplers were labelled so that the same sampler was always used at the same site. Only when a sampler became damaged was it changed, and replaced with a new one.

To collect a surface gas sample from the field or the garden peat core, an inflated sampler was placed within the bucket perimeter and the lid sealed on. A laboratory experiment had previously been set up to determine whether or not a sealed lid gave an effective gas-tight closure. Beginning with a CH_4-C concentration in replicate sealed buckets of 0.48 ppm (900 vpm) and a CO_2-C concentration of 0.43 ppm (800 vpm), 84% of the methane and 97% of the carbon dioxide remained after 48h (allowing for the sample volumes withdrawn). It is possible that some of the loss was attributable to diffusion into the polythene buckets, but a series of laboratory experiments designed to check this produced ambiguous results. It seems likely that most of the loss is due to leakage through an imperfect seal, though a small amount of gas may diffuse into the bucket material. Samplers on dry areas were placed directly on the surface vegetation, but on wet lawns and pools they were taped to the underside of the bucket lid. In June 1982 half the samplers (for each microhabitat) put out in the garden for the monthly peat gas record were taped to the underside of the lid and half were placed directly on the vegetation surface. The results showed no difference in CH_4-C or CO_2-C concentration in the two groups of samplers after the 2d sampling period in any of the three microhabitats (t-test, $p<0.05$).

In the field, the bucket acted as a barrier to the sideways movement of gas originating in the peat outside the bucket, to a depth of 20 cm, into the sampling area, thus minimising the possibility of an unnatural increase in the enclosed gas concentration resulting from bubble evolution as the bucket was approached.

The problem of measuring an unrealistic concentration in the surface samplers, as a result of unnaturally forcing gases out of the peat by approaching closely, did not exist for the garden peat cores because they were contained in complete buckets which were sunk into firm soil.

b) Filling the gas samplers

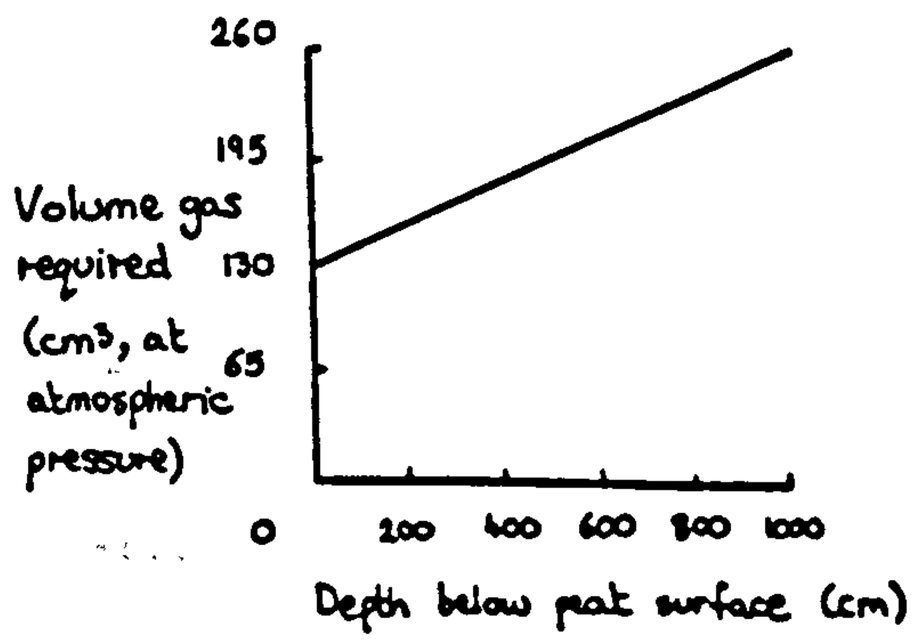
Samplers were filled at the beginning of the sampling period, having first been evacuated. Initially, before a source of N_2 for field use had been arranged, air was used in both garden and field surface samplers and in field deep peat samplers. This was most

unsatisfactory in the latter case, since it introduced oxygen into a generally anoxic system, so from August 1982 all deep samplers were filled with N_2 (BDH, 99.999% purity), as were garden and field surface samplers except in one case: the supply of N_2 ran out on the September 1982 field trip to Moor House, so on this occasion the MH surface samplers were filled with air.

Surface samplers were evacuated using a 60 cm^3 plastic syringe and then sealed with the attached 3-way tap. To evacuate the deep peat gas samplers it was found adequate simply to leave the 3-way tap on the end of the PVC tubing open for a minute or so, such that the pressure of the surrounding peat forced all gases out of the sampler. Plastic syringes (60 cm^3), with 3-way taps attached, were filled with N_2 (or air) from a cylinder (a lecture bottle was used in the field). The samplers were then filled from the syringes with a known volume of gas measured at atmospheric pressure after using the excess pressure to flush the attached 3-way taps to clear away any air contaminants.

The volume of gas used was dependent upon the sampler being filled. It was important to only *just* inflate the samplers; under- or over-inflation could result in a change in the equilibration period as a result of a change in sampler geometry; under-inflation could affect the surface area available for diffusion, whereas over-inflation would change the permeability of the inner. The volume of the sampler inners was 130 cm^3, so this was the volume of gas used to inflate all surface samplers, the volume contained in the 20 cm of PVC tubing (1.4 cm^3) being negligible. The deep peat samplers had to be filled *in situ* with a larger volume of gas, as measured at the surface, to compensate for the additional pressure at depth (Boyle's Law and Fig. 3.3). Once filled, the samplers were sealed off with the 3-way tap

FIG. 3.3 Gas volumes required to inflate buried samplers



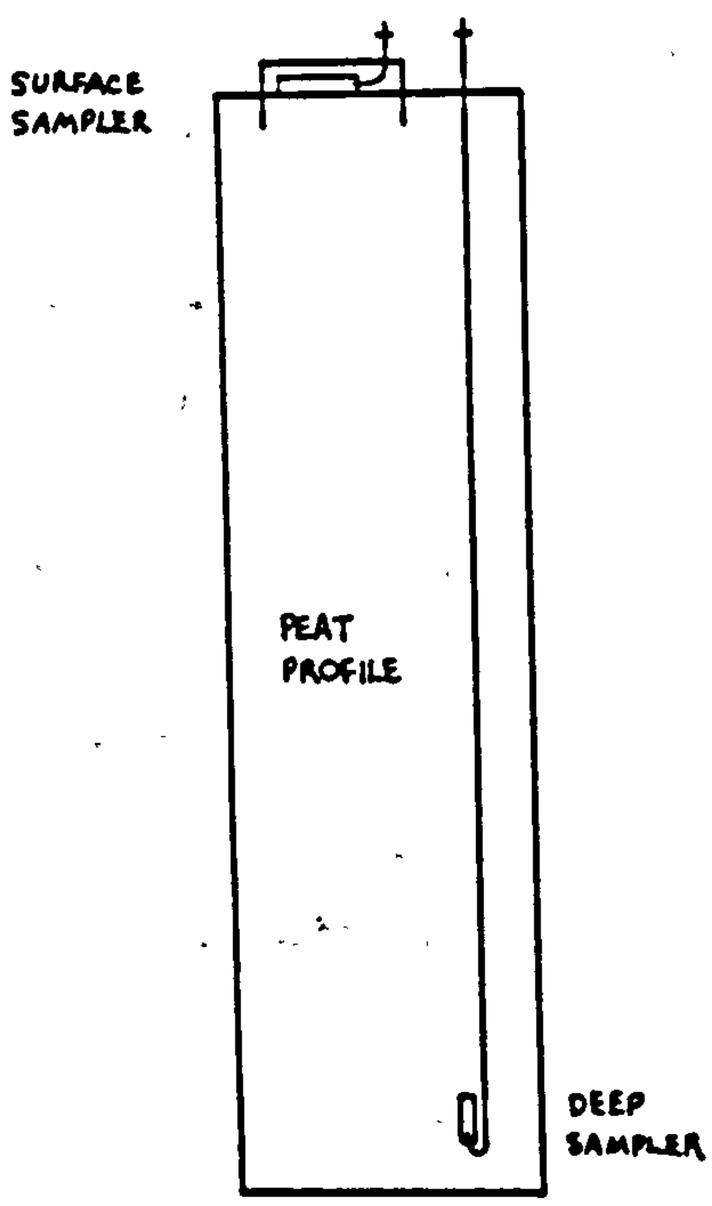
and left for the duration of the sampling period. Because of the additional pressure within the deep peat samplers it was found necessary to clamp the PVC tubing just behind the 3-way tap to seal it fully and prevent gas leaking out over the sampling period.

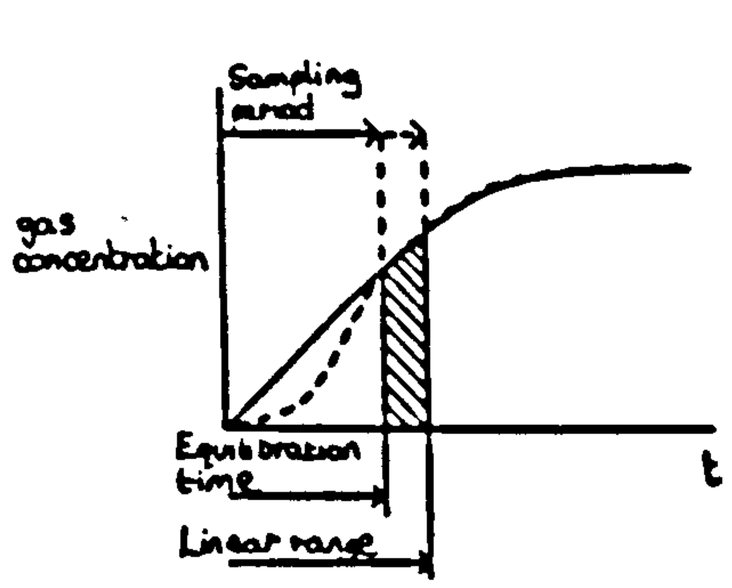
c) Equilibration time and sampling period

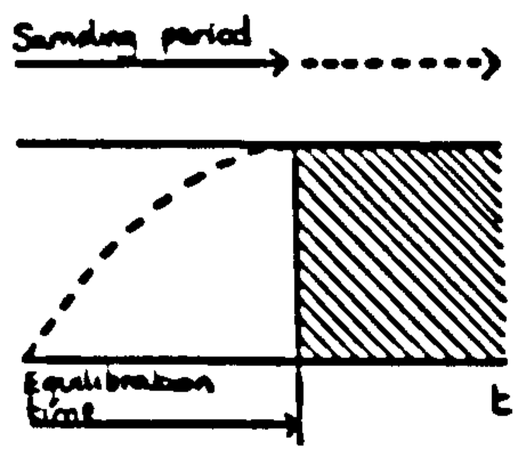
In order to obtain a representative sample of gas, a sample could only be withdrawn when sampler and surroundings were in equilibrium in terms of gas concentration. The time between filling the sampler and that when an equilibrium is first established is here referred to as the equilibration period. A sample cannot be taken within this period if it is to be meaningful. In the deep peat this equilibrium is unlikely to change very much once established, as a result of the relative constancy of the surroundings, so the sampling period, defined as the time between filling the sampler and that when the sample is withdrawn, is less critical, and a sample could be withdrawn after almost any reasonable period beyond the equilibration time. In contrast to this, conditions around the surface samplers, although enclosed, were not constant. The concentration of gases inside the bucket increased with time from when the lid was sealed on. However, once the equilibrium between sampler and enclosed atmosphere was reached, it is unlikely that it would be upset in either direction (except temporarily by sudden erratic bubble evolution), and so long as the increase in the enclosed concentration was linear with respect to time, a sample withdrawn at any given time after the equilibrium had been reached could be used to give the surface flux. In practice, the rate of concentration increase in the enclosed atmosphere does not remain linear indefinitely. It is known, for example, that the net flux of CH_4 begins to slow; this may in part be due to its reoxidation to CO_2 (Dunican & Rosswall 1974; Svensson 1974; Bunnell, MacLean & Brown 1975; Svensson & Rosswall 1984). It therefore becomes important to know the exact shape of the curve describing the increase in concentration with time in the enclosed atmosphere, in order to be able to decide on a sampling period which allows for an equilibrium to have been set up, but is not so long that the concentration increase has ceased to be linear. The differences in absolute sampling period

length, and the degree to which a given sampling period may or may not be allowed to vary between samples, is shown diagramatically in Fig. 3.4.

FIG. 3.4 Difference in equilibration time and sampling period for surface and deep peat gas samplers







Results of experiments (Appendix C) to determine the relative rate of diffusion of CH_4 and CO_2 through the sampler inner, and the time necessary for an equilibrium to be established between the surface samplers and the surrounding atmosphere, showed that within two days an equilibrium was established, and that during this time the surface flux was linear. Two days was therefore adopted as the sampling period for garden and field surface samplers, which made it possible to set out field samplers and collect the surface samples during a single field visit. The sampling period varied between trips by only a few hours.

Because a similar method to that used to determine the equilibration time of the surface samplers would have to be destructive if applied to the deep peat gas samplers, the problem of determining the sampling period here was approached in a different way. Results from gas samples taken from buried samplers after different time periods showed that after about 14 days the concentration of gases inside the sampler did not change significantly over a period of three months. There was no indication that it would have changed after this, but the experiment was stopped at this point. The sampling period for deep peat gas samples was therefore set to a minimum of 14 days, but the exact period appeared not to be critical once the initial equilibration time had passed. Since most field visits were about a week in length, in practice the sampling period for the deep peat samplers was the time between the last day of two successive visits, so that deep samplers were sampled, and refilled with gas, at the end of each visit and were left to equilibrate until the next visit. Consequently, sampling periods were much more variable than those for surface samplers, ranging from approximately five weeks in the field season, to between three and six months over the winter period.

d) Collection of gas samples

At the end of the sampling period in the field the following samples were taken:

i) a sample from each of the deep peat gas samplers

ii) a sample of the enclosed bucket atmosphere around each surface sampler

iii) a sample from inside each surface sampler.

Gas samples corresponding to ii) and iii) were likewise regularly collected from the garden peat cores.

The pairs of surface gas samples collected from within any one bucket acted as a check on whether or not an equilibrium had been reached across the sampler membrane. Of the two, the enclosed bucket atmosphere sample was taken first, via a 20 cm length of thick-walled, narrow-bore PVC tubing which passed tightly through a rubber bung sealed into a hole in the bucket lid. The tubing was fitted with a 3-way tap which remained closed until a sample was taken. Then the lid

of the bucket was removed and immediately a sample was taken from the sampler itself. The samplers and lids were removed between samples.

The deep peat gas samples were taken directly via the tap on the PVC tubing, then this was left open for approximately five minutes to evacuate the sampler, after which the sampler was re-inflated with the appropriate volume of gas and sealed until the following visit.

In every case the samples were withdrawn into a 60 cm^3 plastic syringe, by attaching this to the tap on the sampler tubing. For each of the surface samples, the first 5 cm^3 of gas withdrawn was vented to the atmosphere to flush the taps and syringe nozzle. Deep peat sampler fittings were not flushed, to avoid the possibility of flushing away the entire sample. In most cases, as was expected, the sample volume was approximately 130 cm^3, but there were occasions when only a very small volume could be withdrawn, so it was unwise to risk losing a sample in this way.

3.1.2 STORAGE AND ANALYSIS OF GAS SAMPLES

STORAGE OF GAS SAMPLES

The syringes containing gas samples were sealed using 3-way taps, and were thus transported to London and stored at room temperature in the laboratory without further manipulation until analysis.

The results from laboratory experiments to monitor any change in the component concentrations of stored samples with time indicated that on the whole they did not change significantly over a period of nine days, after which the experiments were stopped. However, 23% of the 215 samples taken over nine days showed a change of >10% of the initial sample concentration, but these values were erratic and the following sample did not usually show a continuation of the trend. An early storage experiment had shown that over a period of five days, the maximum percentage change in concentration compared with the original was 17% for CH_4 and 13% for CO_2. In absolute terms this was equal to 7.14×10^{-4} ppm (1 vpm) and 1.96×10^{-1} ppm (100 vpm), respectively, for CH_4 and CO_2. After the five days a number of samples showed larger changes. Sample collection was therefore

organised so that all samples could be analysed within five days of collection, as a maximum. In practice, the majority were analysed within three days.

Over a five-day period, the storage experiments showed that if the maximum percentage changes in concentration measured at any time during the experiment for each component were added together, that is, if it is assumed that the maximum changes measured for each component occurred together, the total absolute change would be less than 50 000 vpm, or 5% of the total sample volume. Hence, in conclusion, it is evident that some changes may have occurred to samples as they were stored in syringes before analysis. However, such changes are not likely to have been frequent, and in most cases would have been less than 10% for individual component concentrations and less than 5% of the total sample volume. The main results probably do contain a proportion of erratically misleading values, which can be expected to be extreme, and therefore readily apparent.

ANALYSIS OF GAS SAMPLES

Gas samples were analysed using a Perkin Elmer Sigma 3B gas chromatograph (GC) equipped with a dual ⅛" stainless steel column system consisting of a 4 m porous polymer Porapak T column and a 1 m molecular sieve MS13X column. The system was designed to separate the oxygen and nitrogen fractions of air, and a number of lighter hydrocarbons. Helium was used as the carrier gas, at a flow rate of 30 cm^3 min^{-1}. Gas samples were introduced directly from the sample syringes, into a gas sampling valve (GSV) via a small device designed to ensure that the sample was introduced at atmospheric pressure. The GSV was fitted with a 1.0 cm^3 sample loop. Samples were run for 9-10 minutes, after which no more detectable components were eluted.

The chromatograph was fitted with a thermal conductivity detector and a flame ionisation detector, in order to ensure sufficient response to all components for a reliable quantification of the resultant chromatogram. Output was to a Linseis chart recorder (model LS44). The chromatogram peaks were quantified manually using peak

height, following at least daily calibration with standard calibration gas mixtures (Phase Separation, Clwyd).

Details of the GC configuration and operation, and gas sample analysis, are given in Appendix D.

3.1.3 MEASUREMENT OF GAS DIFFUSION RATES THROUGH PEAT

A knowledge of the rate at which gases diffuse through peat is important for a thorough interpretation of the results. Values of diffusion coefficients for gases in air and water exist, but the corresponding values for gas diffusion in peat are lacking. Clymo

TABLE 3.1 Summary of experiments to determine gas diffusion rates through peat.

Date	Peat cores and gas concentrations used			Conc^{n} introduced into end A (vpm)*, stage 2	
	Exp^{t}.	Tube (E/C)*	Peat used	CH_4	CO_2
20/07/83	1	1 (C)	MH Core 1 12-20.5 cm		
		2 (E)	23/06/83 50-64 cm		
		3 (E)	12-18 cm		
29/10/83	2	1 (C)	MH Core 1 12-20.5 cm		
		2 (E)	23/06/83 50-64 cm	181 000	211 600
		3 (E)	12-18 cm	191 800	
08/12/83	3	1 (E)	MH D3 01/08/83 263-271 cm	211 600	212 600
		2 (E)	MH D4 01/08/83 261-275 cm	222 600	226 900
		3 (C)	MH D6 01/08/83 150-175 cm		
18/01/84	3a	1 (E)	MH D3 01/08/83 263-271 cm	218 600	188 600
		2 (E)	MH D4 01/08/83 261-275 cm	213 900	173 100
		3 (C)	MH D6 01/08/83 150-175 cm	220 400	195 300
03/02/84	4	1 (E)	MH D3 01/08/83 263-271 cm	110	340 000
		2 (E)	MH D4 01/08/83 261-275 cm	296 000	5 640
		3 (E)	MH D6 01/08/83 150-175 cm	6 900	5 960
06/03/84	5	1 (E)	MH D3 01/08/83 268-271 cm	355 000	
		2 (E)	MH D4 01/08/83 261-275 cm	354 000	
		3 (E)	MH D6 01/08/83 150-275 cm	340 000	

* E=Experimental
C=Control
* Mean concentration of stage 2

(1984) cites unpublished results giving a value of 500 $cm^2\ y^{-1}$ for CH_4 in peat. Further experiments were carried out during the present study to determine the diffusion coefficients of CH_4 and CO_2 in peat collected from an area immediately adjacent to the MH field gas sampling sites (see Appendix E for details).

Essentially, a known concentration of gas was introduced at one end of the experimental peat core and the subsequent increase in concentration of the gas at the other end was monitored at 24-hourly intervals. The intention was to measure diffusion a) through peat of a given bulk density, comparing results from experiments in which different concentration (gradients) had been imposed, and b) through peat cores of different bulk density, with concentration (gradients) being kept constant between experiments (Table 3.1). Methane and carbon dioxide concentrations used ranged between about 0.1% and 35% (v/v), and so some were high relative to those measured in field peat gas samples. This was intentional, in part to reduce the time needed to run the experiments. In practice, each experiment was monitored for about one month. The experimental details and calculations were rather involved, and have been placed in Appendix E in order not to interrupt the main text here. The results are described in the next chapter.

3.1.4 MEASUREMENT OF PEAT SULPHIDE

Two independent methods were adopted for recording sulphide in the peat. The presence of sulphide at depths down to 30 cm was detected qualitatively from the discolouration of silver-plated brass strips inserted into the peat. Records were made at approximately monthly intervals. In addition, quantitative measurements of total sulphide, giving a point profile of sulphide activity, were taken over the entire peat profile at selected areas in the field adjacent to some of the deep peat gas sampler sites. Details of both these methods and the corresponding records are given in the following sections.

QUALITATIVE SULPHIDE RECORD

a) Method

The method used to identify any zones in the shallow depths of peat where sulphide activity was relatively high, was modified from those of Burgeff (1961), Clymo (1964) and Urquhart (1966). The method gives a visual measure of the distribution of sulphides in the peat by the formation of silver sulphide (Ag_2S) which discolours the surface of the strip, Fig. 3.5a (inside back cover). Brass strips measuring 1.25 x 30 cm were silver-plated (25 μm thickness) on one surface, and one end was sharpened to facilitate its progress through the, often matted, top 30 cm of peat. Strips were left in position in the peat for two days (the same period as for gas sample collection). At the end of this period, when the surface gas samples were collected, the silvered strips were withdrawn, rinsed with distilled water and dried with tissue paper. The discolouration was permanent if the strip was not scratched or cleaned, but the colours became less vivid over a period of weeks.

After making a permanent record of the discolouration (see below) the strips were made ready for re-use by gentle cleaning with "Silvo" silver-cleaning agent and subsequent polishing with clean, dry cotton wool.

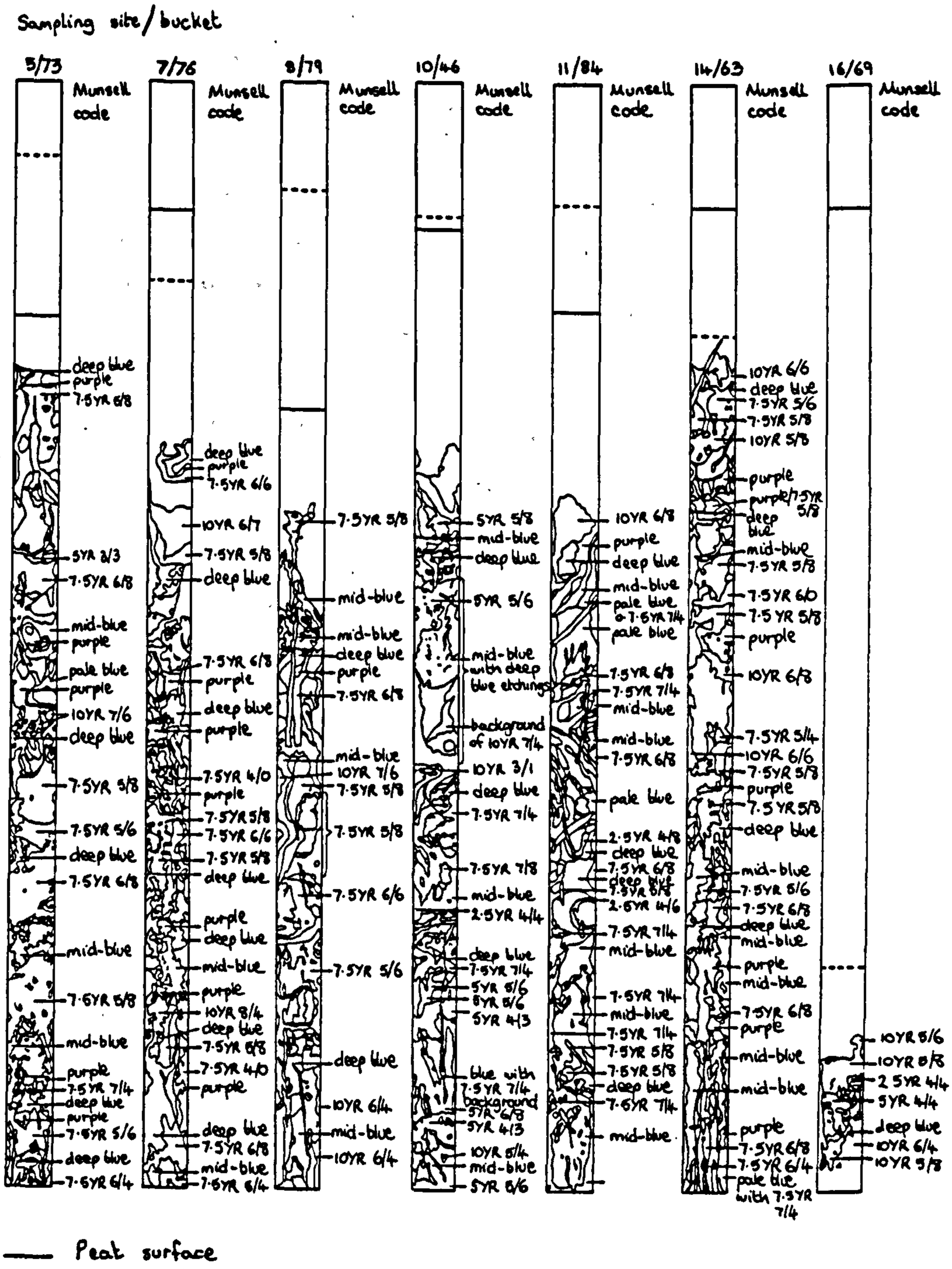
b) Recording methods

It is evident from Fig. 3.5a that the deposition of Ag_2S on the silvered strips results in a complex pattern of many subtly different hues. Records began in May 1981. Each discoloured strip was drawn, detailing all the areas of different colouration and coding them according to the Munsell colour code usually applied to the description of soils. This gave a standardised description, interpretable to anyone with access to Munsell colour charts (Fig. 3.5b).

It was hoped that the discolouration could be 'calibrated' for sulphide concentration, and a series of trials were carried out in which replicate silvered strips were left in (buffered) standardised sulphide solutions covering the range 1 x 10^{-8} to 1 x 10^{-2} mol l^{-1} S^{2-}

FIG. 3.5b Exemplary discoloured silvered strips from field peat.

The corresponding colour transparency (Fig. 3.5a) can be found inside the back cover.- Strips measure 30 cm x 1.25 cm.



for periods of 6, 12, 24 and 48 hours and then removed and the discolouration observed. It was clear from the results that the colours are not correlated with sulphide concentration, and hence it

was not possible to quantify the peat sulphide concentrations from the discolouration. However, the trials established that discolouration is apparent on strips left in contact with sulphide concentrations of 10^{-5} mol l^{-1} S^{2-} and stronger, but none was seen if the solution was 10^{-6} mol l^{-1} S^{2-} or less. Thus the limit of detection by the discolouration technique is 10^{-5} mol l^{-1} S^{2-}, or 0.26 ppm S^{2-}. The results also showed that the weaker the sulphide solution, the longer the discolouration took to reach the point when no further change occurred. For the stronger solutions this was reached within just 6 hours, but in all cases the final colour pattern was observed within 48 hours, the period for which strips were buried in the peat for field and garden sulphide zone determination.

The drawing and coding of the discoloured strips had two disadvantages; it was time-consuming and the final records did not lend themselves to rapid mental reconstruction of the patterned strip. Thus, once it had been established that the absolute hues did not convey quantitative information, a (colour) photographic record was made of all the strips, in addition to the coded drawings. This had previously been avoided because of the difficulty in standardising photographic light conditions and colour reproduction. Now a box was made in which sufficient standardisation of light conditions was possible to be able to take clear photographs of a set of strips together, for comparison. Essentially, it was a wooden box lined with hardboard (rough side innermost), with the inside painted matt white and a hole in one end just large enough to admit the camera lens. A flash unit was mounted in the corner at the same end and when activated, with the box lid closed, its light was directed obliquely across the silvered strips and was diffused by the rough, matt white surface of the box interior. In practice all reflections were not avoided, as had been hoped (see Fig. 3.5a), but conditions were standardised and the photographs were clear. They gave a readily-comparable set of records in which features of possible interest were immediately apparent.

The Munsell coded drawings (recorded May 1981 onwards) and the photographs (taken September 1982 onwards) were used to establish the presence or absence of a sulphide zone, the depth at which it was

first noticeable, and the presence of any identifiable vegetation or gas bubbles in the peat. Previous work has suggested that gas bubbles leave irregularly-shaped, boldly-outlined, clean silver areas (Burgeff 1961; Urquhart 1966), whereas *Eriophorum* plants adjacent to a silvered plate or strip will leave a plain silver area which is linear and describes the outline of the plant due to sulphide-free areas believed to be caused by the diffusion of oxygen from the plant's tissues (Armstrong 1964; Urquhart 1966). In the present study these features were seen (Fig. 3.5a), and several silvered strips were removed which clearly silhouetted an intact section of a *Sphagnum* plant with densely-crowded leaves easily recognisable.

QUANTITATIVE SULPHIDE MEASUREMENTS

a) Introduction

Total sulphide was measured at intervals down the full peat profile using an Orion silver/sulphide (Ag/S) electrode (Orion Research, Cambridge, Mass., model 94-16) and an Orion Double Junction reference electrode (model 90-02) with outer (10% KNO_3) and inner filling solutions provided by Orion (90-00-03 and 90-00-02, respectively). The silver/sulphide electrode responds to free sulphide ion activity within the real concentration range 10^{-7} to 10^{0} mol dm^{-3} S^{2-} (0.003 to 32 000 ppm). The measured electrode potential (E) is dependent on the reference potential (E_o), electrode slope (S) and the sensed (sulphide) ionic activity (A) according to the Nernst equation:

$$E = E_o + S \log A.$$

The sulphide activity is proportional to the free sulphide ion concentration (C_f), the constant of proportionality being an ionic activity coefficient, γ, which itself varies with *total* ionic strength of the solution, I.

$$A = \gamma C_f$$
$$\gamma \propto I$$
$$\text{and} \quad I = 0.5(\Sigma C_i Z_i^2)$$

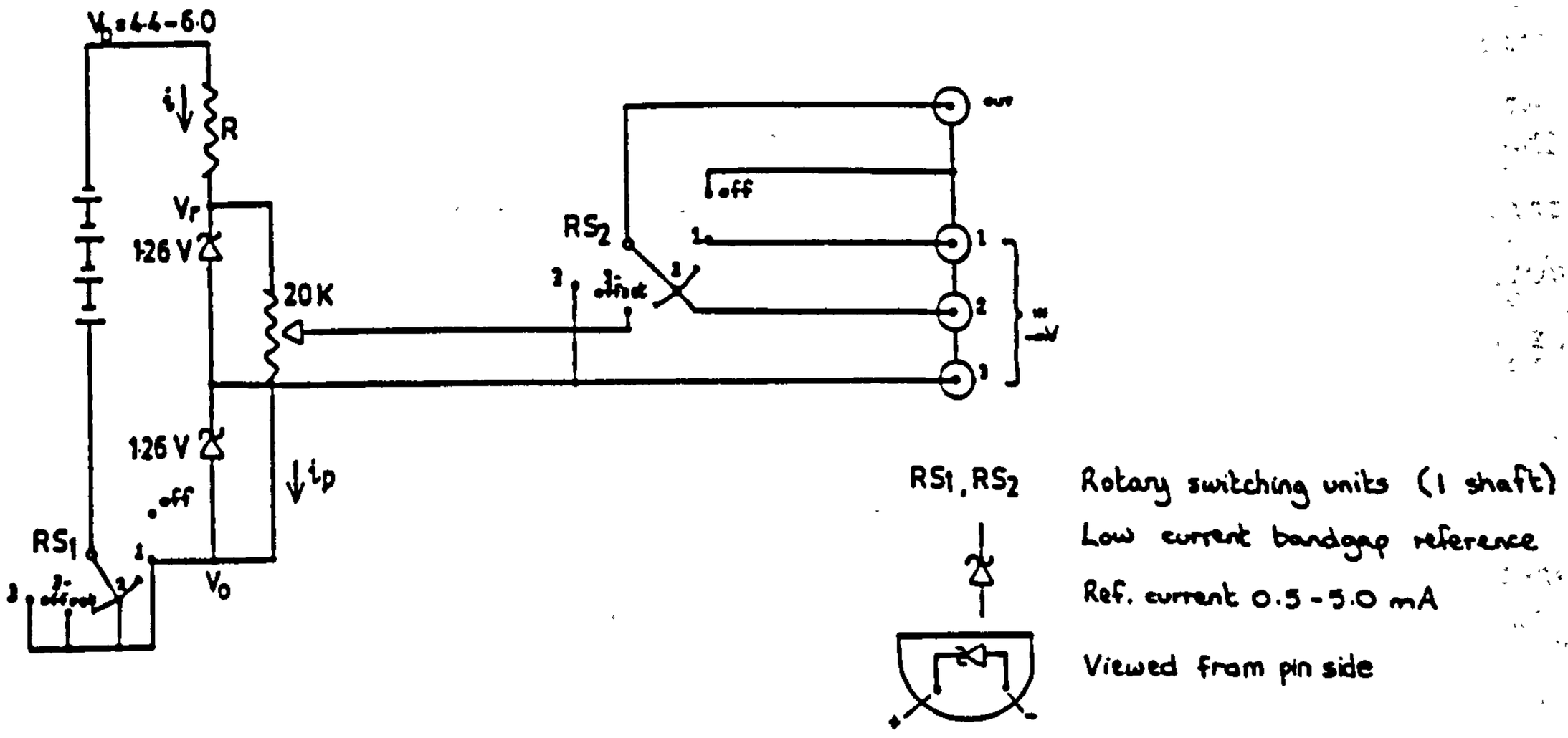
where C_i is the concentration of ion i and Z_i is the charge of ion i.

Hence, if the total ionic strength of the solution being measured is kept high and constant relative to the sensed sulphide ion concentration, the activity coefficient will be constant and the sulphide activity will be almost equivalent to the concentration.

The electrode responds only to free S^{2-} ions in solution; any complexed ions are not measured, and if present will result in an underestimate of the total sulphide ion concentration. Those of significance in peat may include FeS, HS^- and H_2S. The concentration of Fe species in acidic "bog" peat is low; less than 1 μmol dm^{-3} (Clymo 1983, Fig. 4.9, redrawn from Waughman 1980), and at the low pH of this environment, FeS is converted to H_2S and Fe^{2+} ions, the latter of which commonly form humic complexes (Ponnamperuma 1972; Given & Dickinson 1975). Hence Fe is not likely significantly to reduce the concentration of free S^{2-} ions. At the low pH of ombrotrophic peat, most of the S^{2-} is in the form of H_2S. A fuller account of the sulphide-, iron- (II) and hydrogen-ion chemistry in acid peat, as it relates to the measurement of total sulphide ion concentration, is given in Appendix F.

Sulphur anti-oxidant buffer (SAOBII) was added to all sulphide solutions to be measured; both standards and samples. This solution contains NaOH and ascorbic acid. All sulphide is thus converted to the S^{2-} form, the ascorbic acid prevents oxidation and a high,

FIG. 3.6 Circuit diagram used to offset potential difference when measuring field S^{2-} concentrations. The offset sub-circuit is in a closed circuit condition in positions 1, 2 and 3, and functions effectively in position '3-offset' only.



constant background ionic activity is maintained. A laboratory experiment was set up to determine whether the SAOBII itself had any effect on the potential of the sample being measured, and was found not to do so. To take a measurement the Ag/S and reference electrodes were connected to a Pye Unicam portable pH/mV meter (model 293) and placed in the sulphide-buffer solution and after an equilibration period of up to several minutes, the potential difference (mV) was recorded. (The potential difference is large and a part of it was offset using the circuit shown in Fig. 3.6.)

Sulphide solutions were made up in the laboratory and standardised prior to each field visit, during which they were used to calibrate the Ag/S electrode before peat sulphide measurements were taken. The proportion of the total sulphide which was attributable to H_2S was calculated using the equilibrium constant, K, for H_2S and the pH value, which was measured in the peat at the same time as the sulphide. Details of the calculation are included in Appendix F.

b) Standardisation of sulphide solutions for electrode calibration

Deaerated (by boiling for approximately 5 minutes) distilled water was used throughout. A stock solution of sodium sulphide, approximately 4 mol dm^{-3}, was prepared by dissolving about 100 g $Na_2S.xH_2O$ in 100 cm^3 water. After shaking, this was left to dissolve overnight. The stock solution was stored, tightly-stoppered, in a fume cupboard.

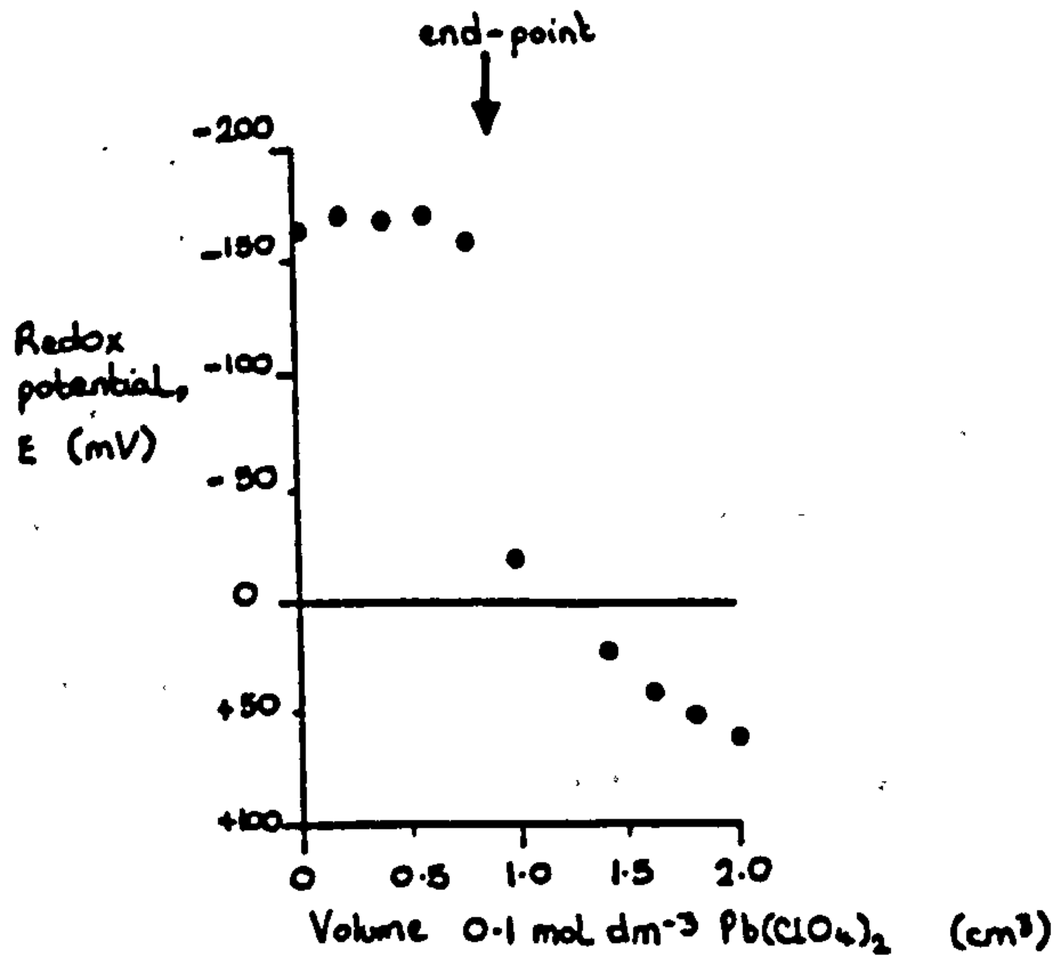
Prior to each field trip, 500 cm^3 of 'weekly sulphide standard' was made up by pipetting 5 cm^3 of stock solution into a 500 cm^3 volumetric flask, adding 250 cm^3 SAOB II, and making up to the mark with distilled deaerated water. Storage experiments on the sulphide standards had shown that weekly sulphide was indeed reliable for a week at least, if the lid of the container in which it was stored was not repeatedly removed and replaced. In order to minimise the possibility of oxidation, therefore, freshly-made weekly standard was thoroughly mixed and then poured into 3 x 125 cm^3 plastic bottles, one for use at each field Site plus one spare; and the remainder into 3 x 15 cm^3 plastic bottles for replicate standardisations in the

laboratory. In each case the bottles were filled until they just overflowed, and the lid, fitted with a rubber seal, was immediately screwed on.

Triplicate standardisations were carried out the same day. The field weekly standards were used within three days. For the field procedure, including the calibration of the Ag/S electrode, see Chapter 3.3, Measurements at and around Deep Peat Sampling Sites.

Initially, standardisation of the weekly sulphide solution was carried out following the method described in the IBP Handbook No. 8 (Golterman, Clymo & Ohnstad 1978, p.173). The method involves the precipitation of S^{2-} as CdS, which is dissolved in an acid iodine solution and then the excess iodine is titrated with $Na_2S_2O_3$ using starch solution as indicator. The whole procedure was time-consuming, and from May 1982 the method described in the instruction manual for the Ag/S electrode was adopted (Orion Research Inc. (1980), Cambridge, Mass., "Instruction manual for the silver/sulphide ion electrode, model 94-16", p.3). This involved a direct titration of standard 0.1000 mol Pb^{2+} dm^{-3} lead perchlorate ($Pb(ClO_4)_2$) (Orion Research, 94-82-06) using the Ag/S and reference electrode pair as the potentiometric end-point indicators. The electrode potential is fairly constant until the end-point, when it suddenly increases (the Ag/S electrode has a negative slope). Aliquots (0.2 cm^3) were added until a further 1.0 cm^3 $Pb(ClO_4)_2$ had been added beyond the end-point. A typical titration curve for 10 cm^3 sulphide solution is shown in Fig. 3.7.

FIG. 3.7 Typical titration curve for standardisation of sulphide solutions



The standardised solution was taken into the field where it was serially diluted for the calibration of the Ag/S electrode. This field procedure is described in Chapter 3.3, Measurement at and around Deep Peat Sampling Sites, as is the measurement of peat sulphide.

3.1.5 MEASUREMENT OF PEAT BULK DENSITY

A total of 12 peat cores, each representing the complete profile at one sampling site in the field, were collected (details in Section 3.3.2) and returned to London in sealed polythene bags in which they were stored in a cold room at 4 °C until analysis. Storage periods ranged from 2-20 weeks. To measure the bulk density, the less well humified core slices were squeezed over a very fine sieve to remove excess peat water without the loss of any biomass; this treatment was omitted for the well-humified slices from the deeper cores. Next, the slices were air-dried in the laboratory for 3-7 days. The peat was then transferred to pre-weighed aluminium foil trays and oven-dried at 105°C for approximately 24 hours. After this the samples were cooled in a desiccator with silica gel as desiccant, and weighed. The oven-drying, cooling and weighing were repeated at daily intervals until the change in weight fell to less than 0.05 g per tray. The total dry weight of each slice was then determined, and the bulk density, ρ, calculated, knowing the volume of the fresh slice:

$$\rho = \frac{\text{dry weight}}{\text{original volume}} \quad (\text{g cm}^{-3}).$$

The results of the analysis are given as part of the field site descriptions (Chapter 2).

3.1.6 INVESTIGATION OF PEAT PROFILE STRATIGRAPHY

A total of 148 peat samples were collected from the field sites, representing complete profiles; details of collection are given in Section 3.3.2. The samples were transported in sealed polythene bags to London and stored at 4°C until analysis. To determine the

composition of the peat, a small volume (roughly 0.25 cm^3) was taken from a sample and mixed to a wet slurry with water. A drop of the slurry was placed on a microscope slide and examined for plant remains, which were classified into the following groups and sub-groups:

i) Vascular plant - *Eriophorum*
- large wood fragments (0.2-0.5 cm diam.)
- small wood fragments, possibly *Calluna* (<0.2 cm diam.)
- *Phragmites*
- unidentified

ii) *Sphagnum*
- Acutifolia section
- Sphagnum section
- Cuspidata section
- Squarrosa section.

No other identifiable plant remains were discovered, but obvious gas spaces and the presence of clay had been noted when the samples were collected.

Each peat sample was used for three slurries, and one drop was examined from each slurry; this was found to be adequate for the present purpose since the method was not intended to give accurate quantitative results but rather a general description of the peat profile in the area used for gas sample collection. The results are given in Chapter 2.

3.2 GARDEN WORK

3.2.1 PREPARATION OF GARDEN EXPERIMENTAL PEAT PLOT

'Experimental peat plot' refers to all the peat installed in the garden at Westfield College for monitoring and experimental purposes. It comprises the 'garden plot' with its arrangement of peat-filled buckets and water top-up and drainage systems, and two adjacent 'minibogs' (M1 and M2), or larger volumes of peat, used for

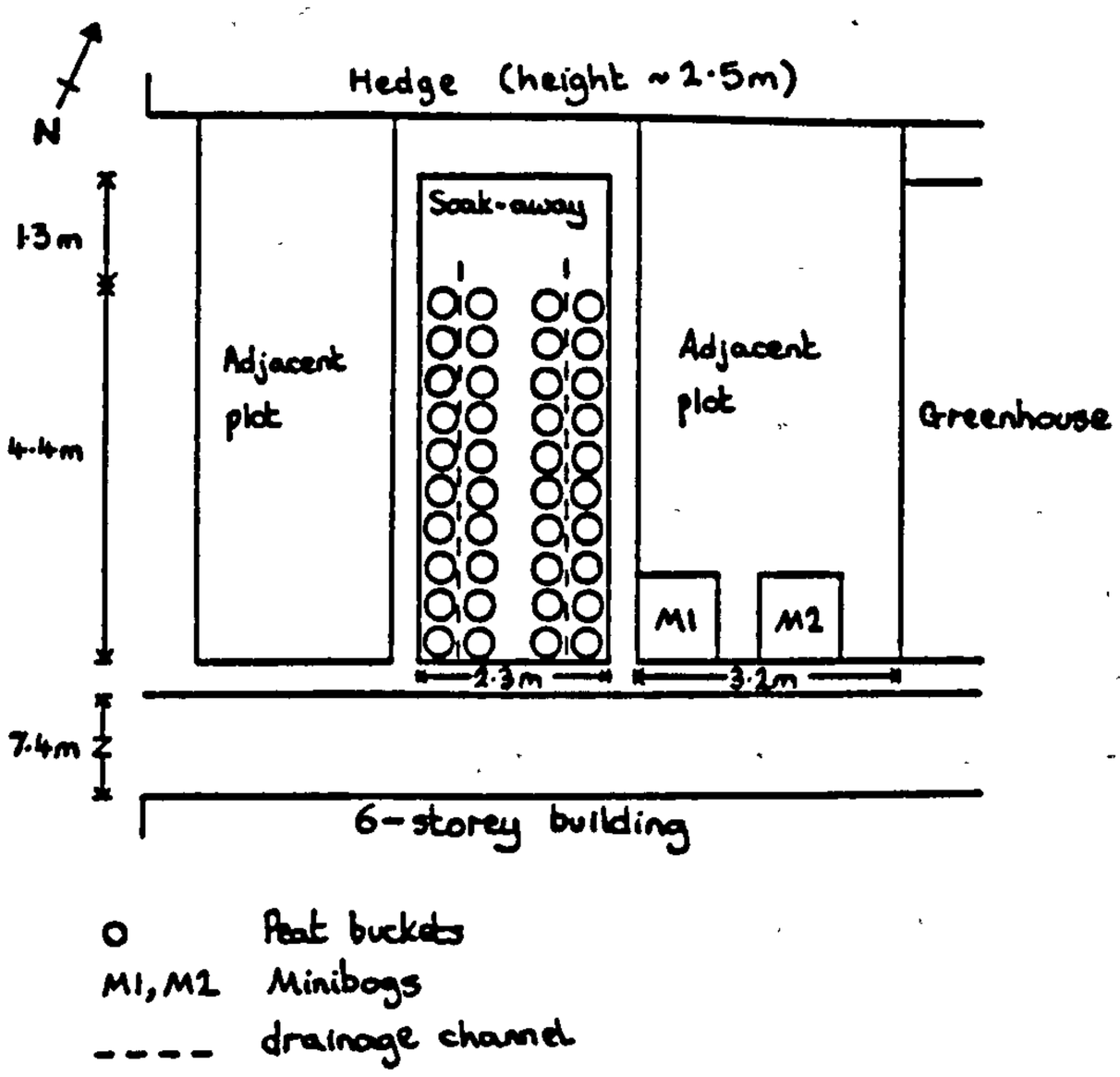
experiments in addition to the regular monitoring programme described below for the experimental peat plot as a whole.

PREPARATION OF GARDEN PLOT

The garden had to be prepared to accommodate the peat cores collected from MH (see Section 3.3.2) to be used for monitoring changes in gas production and the sulphide zone resulting from experimentally imposed water level fluctuations.

In designing the garden plot an attempt was made to ensure that the thermal régime had similar characteristics to that of the climate from which it had been moved. (The change in altitude was from 575 m to less than 80 m.) To this end the peat cores were to be sunk into the ground until their growing surface was flush with that of the surrounding soil. Four rows of ten holes were dug to accommodate the large white heavy duty polyethylene (polythene) buckets (32 cm diameter, 42 cm high, volume ≈25 dm^3; Superfos 25L"S", from Superfos Packaging (U.K.) Ltd., Oakham, Leics.) which were positioned one in each hole to act as liners. These were never moved; they were positioned with a 20 cm gap between their rims between rows, and a 12 cm gap within rows. The position of the plot in the garden in relation to other plots, and buildings, is shown in Fig. 3.8. Shadow

FIG. 3.8 Position and layout of experimental peat plot



from the science building lifted by mid-day. The hedge threw the northern end of the plot into shadow towards the end of the day. The plot was open to its southwestern edge.

The peat cores in the garden plot were intended to be used primarily to study the effects of a fluctuating water level, hence there was built in to the design the means to regulate the water level in them. The system adopted is described below, but in preparing the garden plot it was necessary to make drainage channels to carry away any excess water from the peat. Two such channels were dug; their position is marked by a dashed line (- - - -) in Fig. 3.8. A length of PVC drainpipe, with holes cut in its top side to take upright glass tubes, was laid in the bottom of each channel, and this carried any over-spill from the buckets to a soak-away which was created at the hedge end of the plot (Fig. 3.8). After installing the water level regulation device for each bucket the channels were refilled.

The whole garden plot was protected from cat- and bird-interference by a plastic netting cage, made by supporting the netting on 60 cm-tall bamboo canes. The mesh was of such a size (approx. 1 cm) that it excluded birds but did not significantly affect the light regime inside.

COLLECTION OF PEAT CORES FOR GARDEN PLOT

The collection of the peat cores for installation into the garden peat plot is described in Chapter 3.3.2.

INSTALLATION OF PEAT CORES INTO GARDEN PLOT

The peat cores were transported back to London in the same type of large polythene buckets as were used to line the garden plot holes. Care was taken to keep any disturbance to a minimum. On arrival in London on December 16 1980, the peat cores, in their 'peat buckets', were lowered into the prepared garden plot. Only 35 cores were collected, so one row of liner buckets was left vacant. Initially the cores were not randomised; hummock, lawn and pool cores were located

with their own type. The peat buckets rested in the liner buckets with the rim 10 cm above that of the liners. The cores had been collected as far as possible to leave a 10 cm space at the top of the peat bucket, so that the surface of each core came to lie more or less at soil level when in position.

Once in position the peat buckets were labelled as follows:

12 buckets of hummock peat labelled H1-H12
12 buckets of lawn peat labelled L1-L12
11 buckets of pool peat labelled P1-P11.

The peat had been collected in December while it was still possible to reach the site before deep snow arrived. However, the water level regulation system was only in the planning stage; the final design had not been tested, and hence the necessary equipment was unavailable, until three months later. In the interim, excess water lay on top of the peat cores, and was baled regularly. The plants showed no sign of damage and when finally the excess overflow system was completed at the beginning of April 1981, the peat surface looked none the worse for this treatment.

PEAT BUCKET EXTENSIONS

Presumably in response to warmer temperatures and an extended growing season in London compared to the Pennines, the surface vegetation on the garden peat grew up much faster than had been expected. By the end of June 1981, some *Sphagnum* capitula, particularly at the bucket edges, had grown up above the bucket rim. In these cases it was no longer possible to cover the bucket by sealing any sort of 'lid' onto the rim without damaging the emergent *Sphagnum* plants. It was clear, too, that *Calluna* might cause similar problems in future seasons. It was therefore necessary to extend the peat bucket sides, allowing for a 'lid' to be sealed onto the new rim. A number of trial extensions were tested, but the final design, which was implemented on 25 May 1982, (hummock peat buckets) and 1 June (lawn and pool buckets), was to slide a third, bottomless, 'extension

bucket' inside the peat bucket so that its rim stood proud of that of the peat bucket (by 10 cm). The extension bucket was slipped down inside the peat bucket with the minimum of disturbance to the peat cores. In most cases there was a smell of H_2S as the bucket extensions were fitted, and in some cases peat water was lost from buckets where the water level was high. In this respect the pools suffered the most disturbance of the three peat types.

The full height of the extension buckets was used so that their lower edge came to rest below the water level in even the driest (hummock) peat cores, and effected a satisfactory seal. However, it was still necessary to seal some of the peat-extension bucket joints in those cases where the water levels would come to rest above this in later experiments. Silicone rubber sealing compound was used.

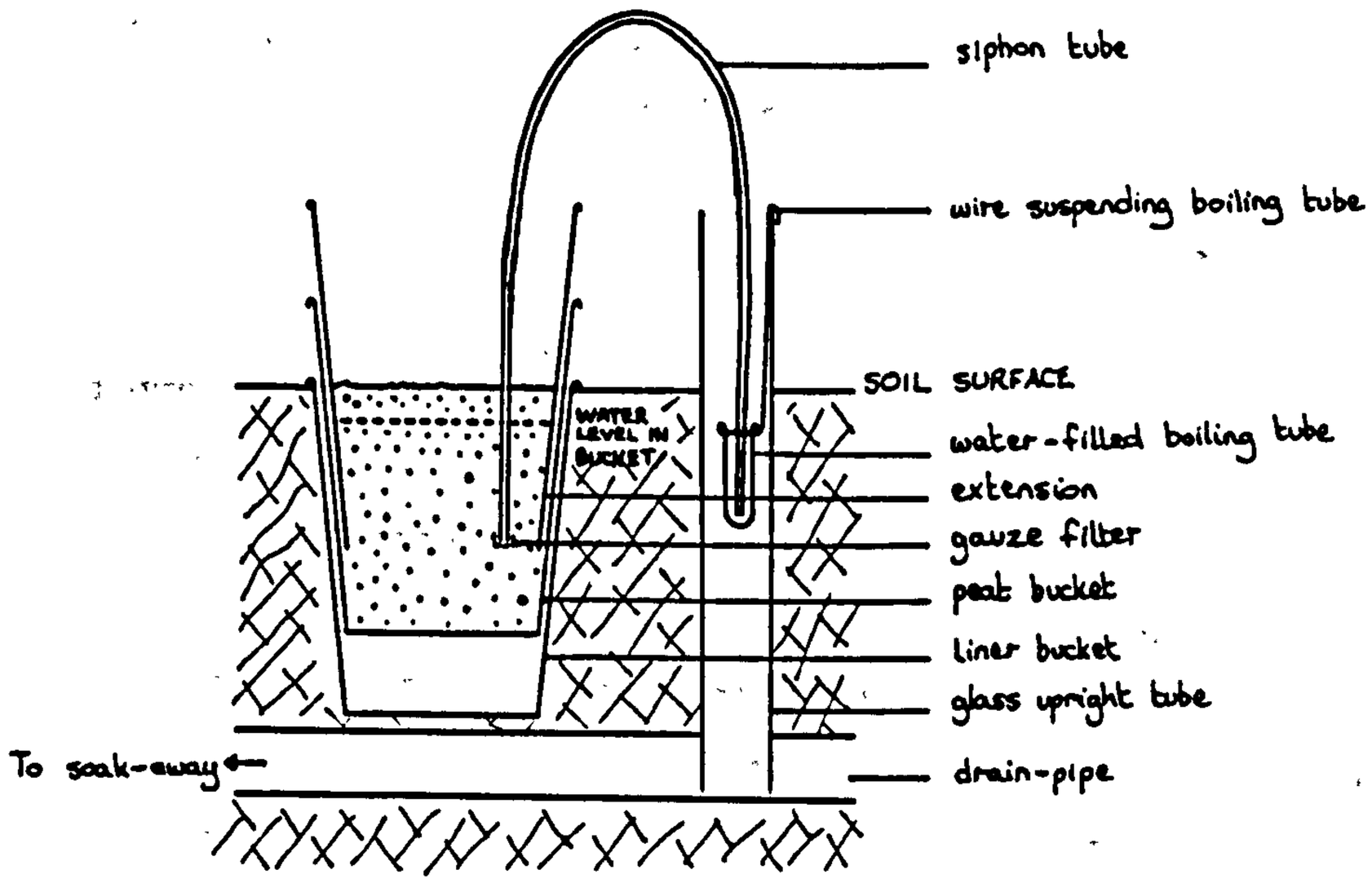
REGULATION OF GARDEN PEAT CORE WATER LEVELS

In order to monitor the effects of changes in the peat core water levels it was necessary to be able to control the water level in the cores very precisely. To this end, each bucket was equipped with a siphoning system to carry away excess water, and a top-up system to restore a falling water level to its required height.

a) Siphoning system

This system siphoned off excess water from all buckets to bring down the water level to the required height. Each bucket had a separate system so that individual water levels could be controlled independently. Fig. 3.9 illustrates the apparatus. The boiling tube was filled with water and suspended in the glass upright tube so that its rim was at the level required for the water level in the bucket. A water-filled PVC siphon tube (O.D. 9.5 cm, I.D. 6.5 cm), fitted at the peat end with a copper gauze filter, was inserted into the peat to a depth well below the required water level, and its other end placed in the boiling tube. When the water level in the bucket rose above the rim of the boiling tube, the excess water was siphoned off and the boiling tube overflowed, the water being carried in the drainpipe to the soak-away.

FIG. 3.9 Siphoning system to carry away excess water from garden peat cores



Maintenance of the system involved regularly checking the siphon for blockages or gas bubbles, either of which might cause it to break, and occasionally cleaning out the accumulated growth of algae from the siphon tube and boiling tube. The gauze filter also needed cleaning occasionally, otherwise partial blockage by small peat fragments slowed down the siphoning.

b) Top-up system

The top-up system was essentially a length of PVC tubing (I.D. 0.3 cm) which ran across the tops of the buckets and was connected to a distilled water reservoir on the fourth floor of the adjacent science building. A small hole was pierced and a hypodermic needle inserted at the point where the tube passed the centre of each bucket. The system was extended to run to the minibogs to keep them from drying up. Minibogs or peat cores could be watered independently, if necessary. The arrangement of the tubing was designed to minimise the pressure drop and ensure that all buckets received water at a sufficient rate to keep their water level at or above the required

height. The distal ends of the tubing were blocked off. Any excess water delivered to the buckets would be siphoned off as described above.

The peat was watered daily during the summer, at other times of the year the boiling tubes were checked daily and the water turned on whenever the water level in them had fallen.

MINIBOGS

The two minibogs M1 and M2 formed the second component of the experimental peat plot. Each is essentially a block of peat collected from the same area in the N. Pennines as were the experimental peat cores. They each measure 1 m x 1 m x 80 cm deep and were installed in the garden in polythene containers lowered into the ground adjacent to the garden peat plot. They were used for monitoring peat temperature and surface gas fluxes. No attempt was made to regulate the water levels in the minibogs beyond keeping them wet enough for the continued healthy growth of the surface vegetation.

3.2.2 SUMMARY OF RECORDS FROM EXPERIMENTAL PEAT PLOT

Table 3.2 summarises all the records made in the experimental peat plot over the study period, and the date when each began.

3.2.3 REGULAR MONITORING IN GARDEN PEAT PLOT

PEAT CORE WATER LEVELS

The peat core water levels are reported as depth below the extension bucket rim (cm, -ve), unless stated otherwise. Measurements which were made before the extension buckets were fitted have been corrected. Relating these measurements to depth below the peat surface is complicated by the surface undulations of a number of the cores, in addition to which the surface of the cores was continually growing upwards (discussed in Section 4.1.4, Water Level Régimes).

TABLE 3.2 Summary of all records made in experimental peat plot. Date of first record is shown, and frequency of subsequent records.

	Cores	M1	M2	Other
Surface gas flux	MF Apr 81	MF Apr 81	-	-
Water level	MF Apr 81	MF Apr 81	-	-
Sulphide zone	M Feb 81	M Apr 81	-	-
Dry wt of new growth	F Nov 82	-	-	-
Temp - peat	D May 83	-	D Jan 81	-
- peat-air interface	-	-	D Feb 81	-
- air	occ thru	-	D Jan 81	-
pH	F Nov 83	-	-	-
Precipitation	-	-	-	D Feb 81
'Significant weather'	-	-	-	D Feb 81

D daily F fortnightly M monthly occ thru occasional throughout
- not recorded

For further details, see text.

The depth of the water level was always measured at the same point on the bucket circumference. Measurements were made at least once a month, on P1, L1 and H1 from April 1981, and on all peat cores at least every two weeks from November 1982 until December 1983, when the garden experiments were completed. Details of the water levels imposed on the cores are given in Section 4.1.4.

PEAT CORE TEMPERATURE

In May 1983 a calibrated thermistor probe was installed in each of P1, L1 and H1 peat cores. All probes were positioned 10 cm above the base of the core. The same (conductivity bridge) meter was used for the probe calibrations and for the garden and field measurements. Records were made more or less daily, at the same time as the morning garden weather records were collected from M2, from May 1983 to January 1984 (Table 3.3, p.99).

PEAT CORE SULPHIDE ZONE

Using the silvered strip method described in Section 3.1.4, Qualitative Sulphide Record, the sulphide zone in peat cores P1, L1

and H1 was recorded for 30 out of 35 months from February 1981 to December 1983. The strip was put as close as possible to the same place each time. The height of the strip relative to the vegetation (moss layer), and to the extension bucket rim was recorded, to enable the position of the sulphide zone to be related to that of the water level. The results are shown in Section 4.4.5, Movement of Sulphide Zone Upper Limit. No quantitative sulphide measurements were made on the garden peat cores because of the destructive nature of the method.

SURFACE PEAT GAS FLUX

Details of the method adopted for collecting surface peat gas samples have been given in Section 3.1.1, Operation of Gas Samplers. The present section explains the design of the garden experiments.

a) Gas sample collection

Between April 1981 and May 1982 surface gas samples were collected from cores P1, L1 and H1 at least once a month. In June 1982 the collection method was improved and from then on gas samples were collected monthly from all peat cores. In December 1982 the water levels in the cores were re-adjusted to compensate for the upward growth of the surface vegetation during the summer and at this point the frequency of samples was increased; until December 1983 gas samples were collected from all peat cores every two weeks. The experiment was divided into three phases, each with a different arrangement of water levels. Each stage ran for between 11 and 16 weeks.

A sample of ambient garden air (at 1.5 m) was collected simultaneously with the peat gas samples, for comparison. Details of the imposed water levels, and all results, are given in Section 4.1.4.

b) Green matter collection

To try to determine the effect of photosynthesis on net surface gas flux, all the green vegetation was removed from half the peat cores (six pool cores). Green matter was cut back to the brown moss layer, woody *Calluna* twigs were left above this, as were dead

Eriophorum leaves. The collected material from each core was dried separately in an oven at 105°C to constant weight (±50 mg).

The initial collection was made in November 1982, prior to the start of the garden experiment; further collections were made immediately before each set of gas samples were taken.

PEAT CORE pH

Because of the disturbance repeated pH measurments would cause in such a small volume of peat, the pH was measured towards the end of the final stage of the garden experiment. The pH at the water level was measured on each of the last four occasions that gas samples were collected; i.e. from 1 November to 12 December 1983. These measurements act as a check on any pH changes which might have occurred in the peat since it was taken from the field. The results are given in Section 4.4.2, pH Profiles.

3.2.4 REGULAR MONITORING IN MINIBOGS

The same variables were monitored in M1 and M2 as in the garden plot, but in addition M2 was used for regular peat temperature measurements.

TEMPERATURE RECORDS

A thermistor probe (for which a temperature/conductivity calibration curve had previously been made in the laboratory) was positioned 30 cm down in M2 on 24 January 1981 and was used to make more or less daily measurements of peat temperature from then until January 1984. A glass bulb thermometer was positioned at the same depth close to the thermistor, and corresponding temperature readings were taken with this to act as a rough check against either the thermistor or conductivity meter giving erroneous readings.

Air temperature 30 cm above M2 surface was measured at the same time as peat temperature using a glass bulb thermometer mounted on a

bamboo cane, shaded from direct sunlight and sheltered from wind by tall vegetation.

Maximum and minimum temperatures at the surface of M2 were recorded more or less daily from 11 February 1981.

MINIBOG WATER LEVELS

The water level in the minibogs was left to fluctuate 'naturally', but was topped up during dry spells to keep the surface vegetation moist. The water level in M1 was measured each time a gas sample was collected from M1, the first record being in April 1981. The water level in M2 was not monitored. Results are given in Section 4.1.4, Water Level Régimes.

MINIBOG SULPHIDE ZONE

The position of the sulphide zone in M1 was recorded as for P1, L1 and H1, using the silvered strip method previously described (Section 3.1.4). Records began in April 1981 and were made throughout the study at the same time as gas samples were collected. The position of the sulphide zone was not monitored in M2. The results are shown in Sectoion 4.4.5, Movement of Sulphide Zone Upper Limit.

MINIBOG SURFACE GAS FLUX

Gas samples were collected from the surface of M1 at the same time as those from the peat cores, beginning in April 1981. No gas samples were collected from M2.

The surface vegetation of M1 was left intact throughout. Gas samples were collected using the same design of sampler as for all other surface samples. An inflated sampler was placed on the surface, and was enclosed by inverting a polythene bucket (25 cm diameter, 25 cm high) over it and pushing the rim of the bucket into the peat until, if possible, it came to rest below the water level, thus effecting a satisfactory seal. To minimise compaction and any resulting disturbance to the peat, a circular slot was cut to take the

bucket rim. This also marked the sampling position. The bottom of the bucket had a hole let into it, sealed by a rubber bung, through which passed a PVC tube (I.D. 2 mm, O.D. 4 mm) to enable the enclosed atmosphere to be sampled without removing the bucket.

3.2.5 CLIMATIC RECORDS

In addition to measuring peat and air temperatures in the experimental peat plot, a number of other climatic variables were recorded regularly.

A rain gauge was constructed adjacent to M1 from a funnel resting in a graduated collecting vessel sunk into the ground, and was used to make more or less daily measurements of the precipitation.

The presence of frost or ice on the surface of the garden peat (cores and minibogs) was also recorded. Notes were made on any 'significant weather', such as hail, snow and high winds.

TABLE 3.3 Frequency of peat temperature and weather records from the experimental peat plot.

a) Garden plot (cores) - peat temperature at ca.-20 to -30 cm; P1, L1 and H1 (thermistor)

First record	05/05/83
Frequency	Daily

b) Minibog (M2) - temperature

	Peat, -30 cm (thermistor)	(thermometer)	Air, +30 cm (thermometer)	Interface, 0 cm (max. + min. thermometer)
First record	24/01/81	26/01/81	27/01/81	11/02/81
Frequency	Daily at ca.0900h and ca.1300h	Daily at ca.0900h and ca.1300h	Daily at ca.0900h and ca.1300h	Daily at ca.0900h

c) Experimental peat plot - weather

	Precipitation	Ice/frost	'Significant weather'
First record	11/02/81	23/02/81	11/02/81
Frequency	Daily at ca.0900h	Daily at ca.0900h and ca.1300h	Daily at ca.0900h and ca.1300h

Table 3.3 gives the frequency of peat temperature and weather records for the entire experimental peat plot, and the first date for which a record is available.

3.3 FIELD WORK

3.3.1 INTRODUCTION

Chapter 2 gives detailed descriptions of Moor House (Burnt Hill) and Coom Rigg, the two field sites used throughout the present study.

Burnt Hill and Coom Rigg are both areas of *Sphagnum-Eriophorum* peat, but CR differs from MH in two important respects. Firstly, a striking hummock-pool topography does not exist, although there are *Sphagnum* lawn areas and drier *Calluna* hummocks; secondly, the basal topography is very irregular, giving rise to areas with different total depths of peat, despite its flat surface.

3.3.2 COLLECTION OF PEAT CORES

CORES FOR EXPERIMENTAL PLOT

A total of 35 cores (12 from hummocks, 12 from lawns and 11 from pools) were taken on 12 and 13 December 1980, from the hummock-pool complex on Burnt Hill which was subsequently used for gas sample collections. Hummock and lawn peat was firm enough to be cut using a stainless steel corer (62 cm high and 32 cm in diameter). The lower edge of the corer was sharpened and two holes in the upper end allowed a tommy bar to be used.

A large sharp knife was used to cut through the matted aerial and root vegetation before the corer was pushed down to cut the core. Twisting was found to damage the peat structure and so was avoided. Once the tommy bar was level with the surface vegetation, the peat around the corer was dug away on one side and the corer then pulled over to allow a spade to be inserted underneath. The tube plus core were drawn out diagonally, the spade preventing the core slipping out. The severed core was cut to the correct length (peat bucket height

minus 10 cm) by placing it on the ground next to its bucket, extruding the extra peat from the bottom of the corer and removing it with the knife. The corer, containing the peat, was then lifted directly over the bucket and the peat allowed to slide down until it came to rest at the bottom of the bucket. The core acted as a loose piston, and air (which escaped slowly) cushioned the descent.

Pool peat was too liquid to be cored, so it was collected by hand. Peat water was lost by this method, as handfuls of peat were lifted from the bottom of the pool into the peat bucket, but the buckets were topped up with pool water afterwards. A layer of live *Sphagnum cuspidatum* was placed on top of the peat, to simulate natural conditions.

At the time of collection, the hummock peat was frozen to about 5-10 cm depth, and most pools had 1 mm or more of ice on them. The field water level was measured whenever a core was collected. The cores, weighing in aggregate approximately 1.5 tonne, were carried over 1.5 km of blanket bog to the nearest road and taken to London where they were installed in the experimental garden plot (see Section 3.2.1).

The surface vegetation of each core reflects the hummock, lawn or pool microhabitat from which it was collected (see Appendix A for microhabitat species).

CORES FOR BULK DENSITY MEASUREMENTS

Duplicate (adjacent) sets of contiguous peat cores representing the entire peat profile from the surface vegetation to the mineral layer at the peat base were collected from areas close to where deep gas samplers were buried. Twelve sets of cores were collected in total, four from MH and eight from CR.

The top 50 cm of each profile was collected using a large cylindrical steel corer similar to that described for the collection of cores for the experimental plot, above, but with a diameter of 19 cm. The large surface area of the corer reduced the compaction which was more likely to occur in the shallower, more open peat than in the well-humified deeper layers. After removing a core, the

surface vegetation was cut off as far as the moss layer and put into a labelled polythene bag. A PVC extruder tube which fitted exactly into the corer was used to push out the core 5 cm at a time and thus cut it into 10 x 5 cm-thick slices with a large knife. To do this most efficiently the corer was lifted onto the extruder tube, which had three vertical rows of holes down it at 1 cm intervals. By putting nails into the appropriate holes the corer could be let down onto them, leaving the peat core itself protruding by the measured amount. The peat slices were put into separate, labelled, polythene bags.

From 50 cm depth to the base, a Russian pattern borer was used to sample the peat. Each 50 cm-long peat core thus collected was cut into 5 x 10 cm cores, which were again bagged separately and labelled. The diameter of the semi-circular cross-section of the chamber was 3.6 cm.

The peat cores were returned to London where they were stored at 4°C until required. The fresh volume of each core was known, so the bulk density of the peat at each depth could be determined from the oven-dry weight. The procedure is described above (Section 3.1.5, Measurement of Peat Bulk Density). Results are given in Chapter 2.

CORES FOR STRATIGRAPHICAL ANALYSIS

A Russian pattern borer was used to collect peat samples from the entire peat profile at representative areas at MH and CR. Contiguous 50 cm cores were extracted, and field notes made immediately on the colour, texture, state of humification, any large gas spaces and any obvious species in the whole core, noting the depths at which the features occurred. Then a sample of all the visually different peat types was collected and put into separate, labelled, polythene bags.

Samples from duplicate profiles at each of two sites at MH were collected, and samples representing four out of five of the CR sites. The vegetation (*Eriophorum* leaf bases and roots) was matted to such an extent at site 16 that it was not possible to use the Russian pattern borer or a large knife.

The samples were returned to London and stored in the polythene bags at 4°C until analysis, the adopted procedure for which is outlined above in Section 3.1.6, Investigation of Peat Profile Stratigraphy. The results are given in Chapter 2.

3.3.3 ARRANGEMENT OF PEAT GAS SAMPLERS

This section describes how and where the gas samplers were positioned at the field sites.

SURFACE GAS SAMPLERS

As described in Section 3.1.1, Operation of Gas Samplers, above, surface gas samplers were put out at the beginning of each field trip into bottomless polythene buckets which were left in place at each field Site to mark the sampling sites. The buckets were positioned on 2 May 1982 (CR) and 4 May 1982 (MH), and replaced the stainless steel collars which had been used prior to this. The positions of the surface sampling sites are indicated in Figs. 2.2 and 2.5.

TABLE 3.4 Total peat depths at field sampling sites.

	Site	Total peat depth (m) A	B	C
MH	1	3.1	2.9	3.0
	2	2.9		
	3	3.4	3.2	3.0
	4-6	3.4	-	-
	7-9	3.0	-	-
	10-12	3.2	-	-
CR	13	4.0	3.8	4.8
	14	5.0	4.6	4.6
	15	4.2	3.5	4.2
	16	3.0	-	-
	17	2.0	1.3	1.6

A Original probing September 1981
B From cores collected for bulk density determinations
C From cores collected for stratigraphical examination
Cores B and C collected immediately adjacent to sampling sites

At MH buckets were set out in pairs. Each member of a pair was positioned directly next to its partner bucket. In total, 18 buckets were placed in three groups of six, each group of six being made up of one pair in each microhabitat (pool, lawn, hummock). At MH the surface samplers were not immediately adjacent to the deep peat sampler sites, but all samplers were within an area of 40 m x 40 m in the same hummock-pool complex.

At CR, in the absence of such a well developed hummock-pool complex, pairs of buckets were placed in the two major microhabitat types; wet lawns and drier hummocks. At the anomolous site 17, situated in the peat lagg, all four buckets were placed in the same wet *Molinia-Polytrichum* marginal vegetation. A total of 20 buckets, two pairs at each of five sites, were used. Sites were positioned over a range of total peat depths from 2-5 m, as shown in Table 3.4.

At both MH and CR the green vegetation was removed from one bucket of each pair down to, and including, the living moss layer, to determine the effect of this component on the gas flux. All buckets were individually labelled, and always the same one of each pair was clipped.

DEEP PEAT GAS SAMPLERS

a) Positioning in the peat

Deep peat gas samplers were buried in the peat on 29 September 1981 (MH) and 30 September 1981 (CR) and are still in position at the time of writing (1988). They were buried using a steel piston borer of essentially the same design as that shown in Fig. E.1, (p.435), but with an internal diameter of 4.2 cm and an internal chamber length of 19.7 cm. In addition, the borer had a fin running vertically down one side of the casing to anchor it in the peat and allow the piston to turn independently inside the casing when necessary.

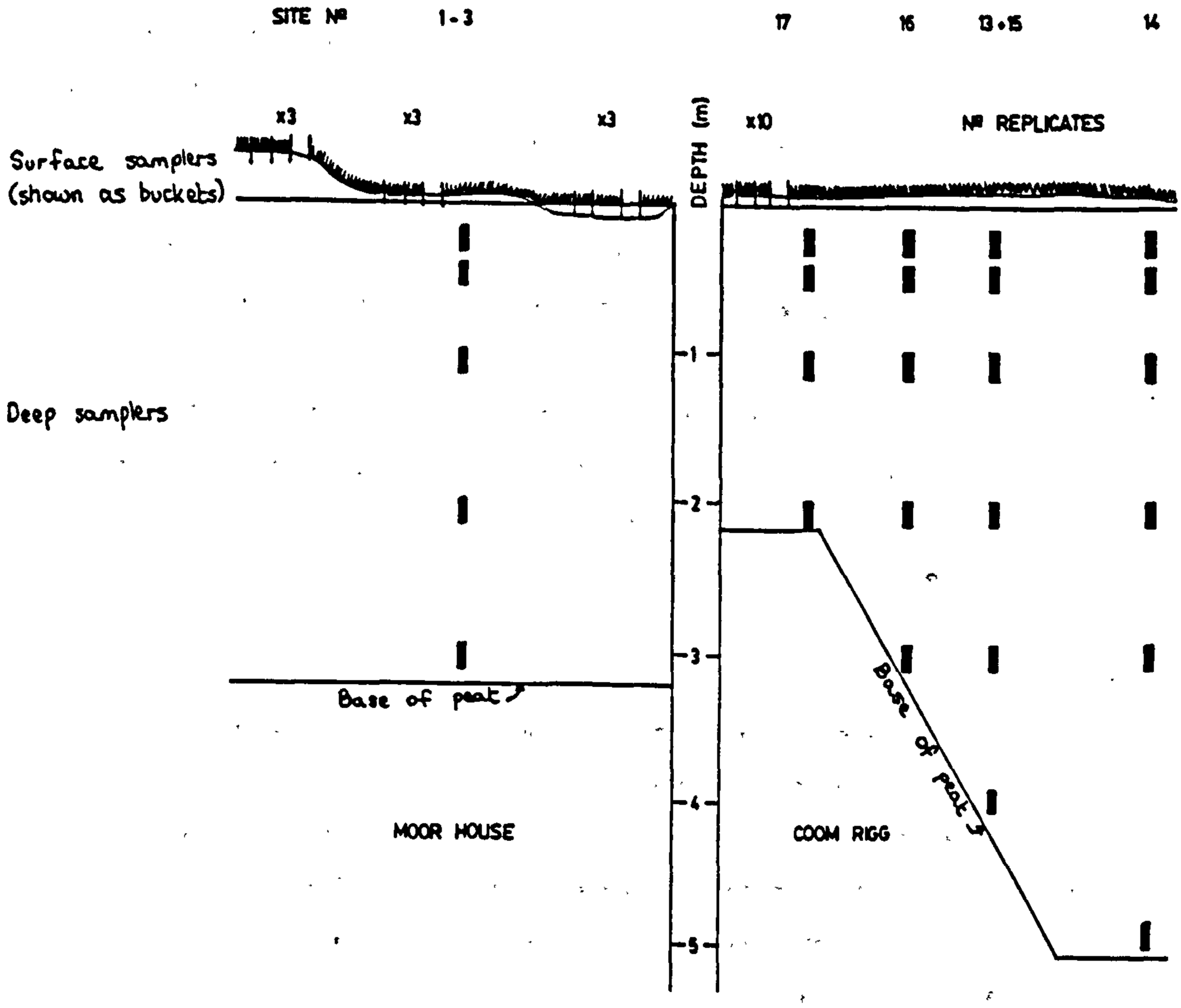
To position a sampler, the piston head was screwed back to the top of the chamber and a deflated sampler inserted. The borer and sampler were pushed into the peat via a prepared hole through the matted shallow layers, and forced down using extension rods until the bottom of the borer was at the depth where eventually the top of the sampler would be. The tommy bar was then turned, while pressure

continued to be applied downwards, to screw the piston down so that the sampler was pushed out of the chamber and into the fresh peat immediately below. The borer was then pulled up, ensuring that it did not catch on the PVC tubing from the sampler and pull it out of position. The sampler could then be inflated.

b) Sampler depths

A group ('string') of samplers was buried at each of three sites at MH and five sites at CR. Each string was arranged to collect gas from a range of depths over the entire peat profile from 0.2 m to the

FIG. 3.10 Peat gas sampler arrangement at Moor House and Coom Rigg. Diagrammatic.



base of the peat. Samplers were spaced more closely towards the top of the profile since it was assumed that gas production was likely to

be more variable there, both with time and depth, than further down where conditions are more stable. It was not possible to position samplers directly above one another without causing disturbance to the peat around all but the deepest, so samplers in any one string were buried within an area of approximately 50 x 50 cm.

The samplers in each string were positioned as illustrated in Fig. 3.10. The Figure is diagrammatic. The positions of the sampling sites at MH and CR are shown in Figs. 2.2 and 2.5, respectively.

3.3.4 FIELD MEASUREMENTS

MEASUREMENTS AT SURFACE SAMPLING SITES

a) Surface and air temperatures

Ambient air temperature was measured whenever surface gas samplers were put out or gas samples collected, using a mercury thermometer held in the hand at about 1.5 m above the ground and sheltered from wind, rain and (occasionally) sun. From May 1983 additional temperature records were made at the same time, following the installation of maximum and minimum and soil thermometers at both MH and CR.

At MH the extra thermometers were placed amongst sites 4-6. The maximum and minimum thermometer was placed with its bulb shaded and 5 cm above an (open) moss cover on a hummock. Three mercury thermometers were mounted singly on bamboo canes and were placed one in each of a pool, lawn and hummock, with the bulb just below the moss (or water, in the case of the pool) surface. In the latter case it was often necessary to adjust the position of the bulb on arrival because of the fluctuating water level.

At CR the maximum and minimum thermometer was placed at ground level at site 13; soil thermometers were put at 5 cm depth at sites 13 and 17 to record any difference in peat temperature between the centre of the bog and the lagg.

b) Water level

The height of the water level inside the bottomless buckets was measured, relative to the bucket rim, each time a gas sampler was put

out. Repeatedly putting pressure on the buckets to seal on the lids resulted in their gradual downward movement into the peat; this was more marked the softer the substrate (i.e. P>L>H). It was occasionally necessary to pull the buckets up again.

After some time it was noticed that the water level inside and outside the buckets could differ; a result of the barrier to lateral movement of water presented by the buckets. So, from October 1982 both water levels were recorded to quantify the effect.

c) Sulphide zone

From March 1982 the silvered strip method (Section 3.1.4. Measurement of Peat Sulphide) was adopted to record the height and extent of the sulphide zone in the peat from which surface gas samples were collected. At both MH and CR, on all field visits except one (a different one for MH and CR) silvered strips were put into the peat in selected buckets when the surface gas samplers were put out, and were collected two days later when gas samples were taken. Twelve 30 cm strips were used, one in each of the nine buckets in which the surface vegetation was intact at MH, and a total of three at CR in (intact) buckets at sites 13, 14 and 16. The height of the top of the strip was measured relative to the bucket rim so that the position of the sulphide zone could be related to the water level in the bucket. On retrieval, the strips were gently patted dry and wrapped in tissue for transport to London, where they were drawn, Munsell-coded, and photographed.

d) Surface peat gas flux

Inflated gas samplers were put out, one in each bucket, and the bucket lids sealed on, for two days during each field visit from May 1982 to September 1983. At the end of the sampling period a gas sample was withdrawn from i) the atmosphere inside the bucket around the sampler, and ii) from inside the sampler, to enable the net flux of peat gases from the peat surface to be estimated. The double set of samples from each bucket allowed a check on the efficiency of the method, which depends on an equilibrium in gas concentration being reached across the sampler membrane. Gas samples were collected,

transported and stored in plastic syringes sealed by 3-way taps, until analysis.

Details of the individual procedures involved in surface gas sample collection have already been given in the Laboratory Work section of this chapter.

With each set of surface gas samples was included an extra one of the ambient gases from about 1.5 m above the bog surface at both MH and CR, for comparison with the enclosed gas concentrations. The ambient sample was simply drawn into a syringe when the other samples were collected.

MEASUREMENTS AT AND AROUND DEEP PEAT SAMPLING SITES

a) Peat temperature

In May 1983 thermistors were placed at 30 cm and 100 cm depth in the peat at MH in the area of sites 4-6, and at the same depths at each of site 13 and site 17 at CR. Unfortunately, they proved unreliable, so none of the data collected from them could be used. Peat temperatures will be estimated from the measured surface temperatures and the damping depth effect recorded over 5 cm depth in the field and 34 cm in the garden minibog M2.

b) Water level

On all field visits between September 1981 and September 1983 at least one peat block was removed at MH and at CR for detailed profile measurements (see c), below). On each occasion, the depth below the surface to which water back-filled the holes was recorded relative to the moss layer. In addition, a rough measure of where the darker, very humified peat (red-brown horizon) began was made. With the well-documented (e.g. Ingram 1983) problems of measuring peat water levels by such methods in mind, these can only be used in this context as a rough guide to the seasonal fluctuations in the water level, especially since blocks were not all cut from the same area. These records were rather intended to help with the interpretation of the sulphide and redox profile results.

c) Redox potential, pH and sulphide profiles

General procedure

From September 1981 profiles of redox potential, pH and sulphide concentration (strictly, activity) were measured in the field at MH and CR on all field visits. Measurements were made at 2-3 cm intervals over the first 20-30 cm, at 25 cm intervals between 25 cm and at least 150 cm, then at 50 cm intervals to the base of the peat. The more frequent surface (≤30 cm) measurements were made on a peat block measuring roughly 20 x 20 x 20-30 cm deep, removed intact from the bog with a spade. Immediately the block was removed, samples (ca. 6 cm^3) were taken at the required depths, starting at 2 cm, from peat inside (unoxidised). This was mixed 1:1 with SAOBII (anti-oxidant buffer, see Section 3.1.4, Quantitative Sulphide Measurements). The resultant slurry was used to measure sulphide activity (see Measurement of Sulphide Activity, below). Redox potential was measured as soon as the peat-SAOBII slurry had been mixed, from another face of the block. The platinum electrode was placed directly into the peat and twisted to and fro a few times to clean its surface. It was then removed and replaced, pushing it in slightly further to expose a fresh peat surface. This was repeated once or twice until a steady, reproducible reading was achieved. When all the redox measurements on the peat had been made, the glass electrode was used to measure the pH. All measurements on the peat block were made at the same depths, and all were made relative to the double junction reference electrode.

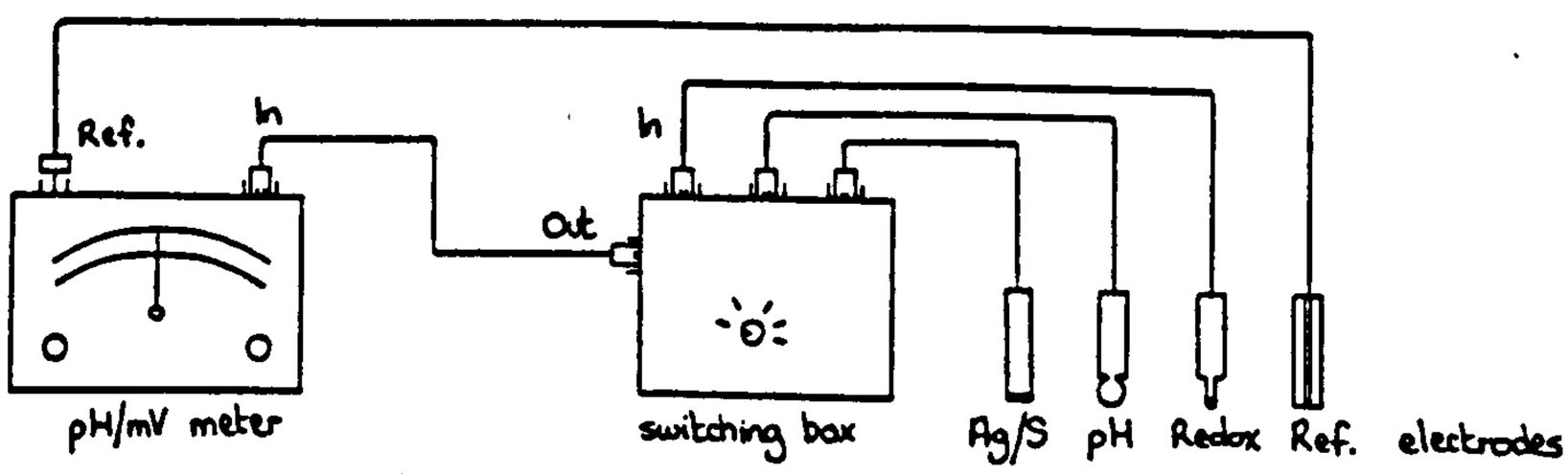
Deeper peat was sampled using a Russian pattern borer and measurements made on each core in the same way; samples were removed immediately to be mixed with SAOBII for sulphide measurement, and redox measurements were made directly afterwards. pH measurements were unlikely to change significantly over a few minutes, and were measured last. Because of the relatively small volume of peat from any one depth which is brought up by the borer (approx. 5.1 $cm^3\ cm^{-1}$) and the problem of oxidation when trying to make accurate records of sulphide activity and redox potential, each measurement on the deeper peat had to be made at a slightly different depth to ensure that fresh, unoxidised peat was used. pH readings are less likely to be

affected, but they too were measured on a fresh area of the core to avoid the risk of SAOBII contamination.

Readings of redox potential (mV), pH (pH units) and total sulphide ion activity (mV) were all made using a portable Pye Unicam pH/mV meter, model 293. The double junction reference electrode was involved for every reading, so this could be left connected to the meter throughout. However, it would have been necessary to repeatedly connect and disconnect the measuring electrodes from the meter and this was undesirable, not only because of the inconvenience, but also because slight changes in the connections might affect the calibration, resulting in measurements not being comparable from one block or core to another. In addition, the needle deflection caused by the sulphide ion potential was well off-scale, and could not, therefore, be measured using the meter as it was.

To solve these problems a 'switching and offset box' was built. All three measuring electrodes were connected to this via independent sockets and were connected to or disconnected from the circuit by a switch. When switched in to the Ag/S electrode socket ('3-offset'),

FIG. 3.11 Apparatus for measuring redox potential, pH and sulphide concentration profiles



the internal voltage of the pH/mV meter was offset by an opposing voltage incorporated into the switching box, thus bringing the deflection back on-scale without changing any connections on the meter. Fig. 3.11 illustrates the apparatus. The circuit diagram for the box is shown in Fig. 3.6, above.

Measurement of sulphide activity

The following procedure was carried out in the field. Redox potential was measured with the meter in mV mode and the switching box at position 1. Free sulphide ion activity in the peat was measured using the slurry prepared from the peat block or core, as described above (General Procedure). Firstly the Ag/S electrode had to be calibrated. Calibration was carried out immediately before and after each day's profile measurements to check any drift of the meter or electrode response. After connecting all three measuring electrodes and the reference electrode, as illustrated in Fig 3.11, the meter was calibrated for pH (position 2) using a buffer solution of pH4 and a check-buffer of pH7.

Following this the electrode slope for sulphide (position '3-offset') was checked by measuring the potential of three solutions in the following order: i) 100 cm^3 H_2O + SAOBII (1:1); ii) i) + 1 cm^3 weekly standard sulphide solution (see Chapter 3.1.4, above, Quantitative Sulphide Measurements); and iii) ii) + 10 cm^3 weekly standard. The electrode slope is expected to be -28 ±2 mV for every 10-fold increase in sulphide concentration.

The Ag/S electrode was then calibrated using three solutions prepared by serially diluting the weekly sulphide standard with SAOBII + H_2O. To prepare the field standards 1 cm^3 of weekly sulphide standard was measured into a beaker. This was made up to 100 ml with SAOBII + H_2O. A second dilution was made in the same way, replacing the original standard with the first-dilution field standard, once this had mixed thoroughly. Thus three standards were used for the calibration: (original) standard (ca. 0.04 mol dm^{-3} S^{2-}), weekly standard x 10^{-2} and weekly standard x 10^{-4}. Each standard was further diluted 1:1 with SAOBII + H_2O before being measured. Beginning with the weakest standard, the Ag/S and reference electrodes were placed in the solution and gently agitated. The switching box was switched to the '3-offset' position and a reading taken once the needle had settled. Each standard was similarly measured, finishing with the most concentrated. The calibrations were repeated at the end of the profile measurements, including that of the meter with the pH4 and pH7 buffers. From the results a calibration curve was produced and used

to convert the peat sample (slurry) readings to sulphide concentrations.

To measure sulphide concentration in the peat the electrodes were rinsed in distilled deaerated water and blotted dry, then placed in the prepared peat slurry. The stable reading was recorded. Results are given in Section 4.4.4, Sulphide Concentration Profiles.

The principle on which the Ag/S electrode operates is described in the Introduction of the Quantitative Sulphide Measurements, Section 3.1.4.

d) Deep peat gas concentrations

Gas samples were collected from each of the samplers buried at MH and CR (41 in total, see Arrangement of Peat Gas Samplers, above, for details) at the end of each field trip, having been inflated with N_2 (or air) at the end of the previous visit. The sampling procedure is given in Section 3.1.1, Operation of Gas Samplers. Samples were collected on 14 occasions between September 1981 and September 1983. Results are given in Section 4.3.

CHAPTER 4

RESULTS

As this is one of those deep observations which very few readers can be supposed capable of making themselves, I have thought proper to lend them my assistance ...

Henry Fielding, *Tom Jones*

RESULTS

4.1 BACKGROUND

4.1.1 INTRODUCTION

This chapter reports all the results from the experimental and monitoring work in the garden and the field. The results of laboratory tests of methodology are largely dealt with elsewhere, but if appropriate, have been included here.

The design of the monitoring and experimental programmes deliberately included various sampling elements for contrast (field and garden; pool, lawn and hummock; different total peat depths). To investigate the factors of importance within each of these necessitated a large number of comparisons between results. For example, in the case of the garden surface gas flux results, the following data sets were analysed and the results compared:

Uncut controls (P,L,H,M1)	- for seasonal effects (within microhabitats)
Cut controls (P vs L vs H)	- water level effect (between microhabitats)
Uncut controls (P,L,H) vs Uncut experimentals (P,L,H)	- water level effect (within microhabitats)
All uncut cores (P,L,H,M1)	- relative importance of temperature and water level (within microhabitats)
Uncut controls (P,L,H) vs Cut controls (P,L,H)	- effect of cutting on seasonal effect (within microhabitats)
Uncut controls (P vs L vs H) vs Cut controls (P vs L vs H)	- effect of cutting on water level effect (between microhabitats)
Uncut experimentals (P,L,H) vs Cut experimentals (P,L,H)	- effect of cutting on water level effect (within microhabitats)
All uncut cores (P,L,H) vs All cut cores (P,L,H)	- effect of cutting on relative importance of temperature and water level effects (within microhabitats)

Within these general data sets sub-sets were formed for some analyses according to the air temperature when the samples were taken, or according to significantly different experimental treatments. The

above comparisons were made for CH_4-C, CO_2-C (and O_2) flux. Similar analyses were carried out on the field data, with the necessary changes resulting from the absence of control areas (with respect to water level). In addition, field data were analysed for differences between Sites (MH & CR), and between sites (4-6, 7-9, 10-12 at MH and 13-17 at CR). The latter comparisons incorporate any effects of total peat depth. Furthermore, CH_4-C : CO_2-C ratios were investigated from garden and field data.

This is a general outline of the analyses involved in investigating temperature, water level and, in the field, total peat depth effects on surface gas flux. Similar seasonal, microhabitat, site and depth comparisons were carried out on CH_4-C and CO_2-C concentration profiles, pH, redox potential and S^{2-} concentration profile data from the field, and the results were compared with any analogous ones from the garden.

The analytical design has been retained to a great extent in reporting the results, for clarity and to help comprehension of the factor or factors under investigation and the data set and statistical approach used. The layout is therefore somewhat mechanical. Further, the large number of statistical analyses involved (>>1000) generated many more results, and necessitated selectivity in reporting them. Therefore, where possible, at the least a summary table of results is shown and comment is restricted, in the main, to those features which appear to be either statistically or ecologically noteworthy.

Fig. 4.1 gives a summary chronology of installations and sampling in the garden and in the field. Table 3.2 indicates when different records began; they were continued until December 1983. The general stratigraphy of the cores can be inferred from the profiles shown in Fig. 2.3. The detailed stratigraphy of individual peat cores installed in the garden was not investigated because of the disturbance this would have caused.

The field results are based on data collected from MH and CR between November 1981 and September 1983 but, as can be seen from Fig. 4.1b, improvements were made to the sampling methods at intervals until September 1982. Hence, not all data are directly comparable. Incompatible values have been omitted from analyses. On only one

FIG. 4.1a Installation and sampling chronology for garden monitoring programmes. Hatching denotes period in which water levels altered and then allowed to settle; no gas samples collected.

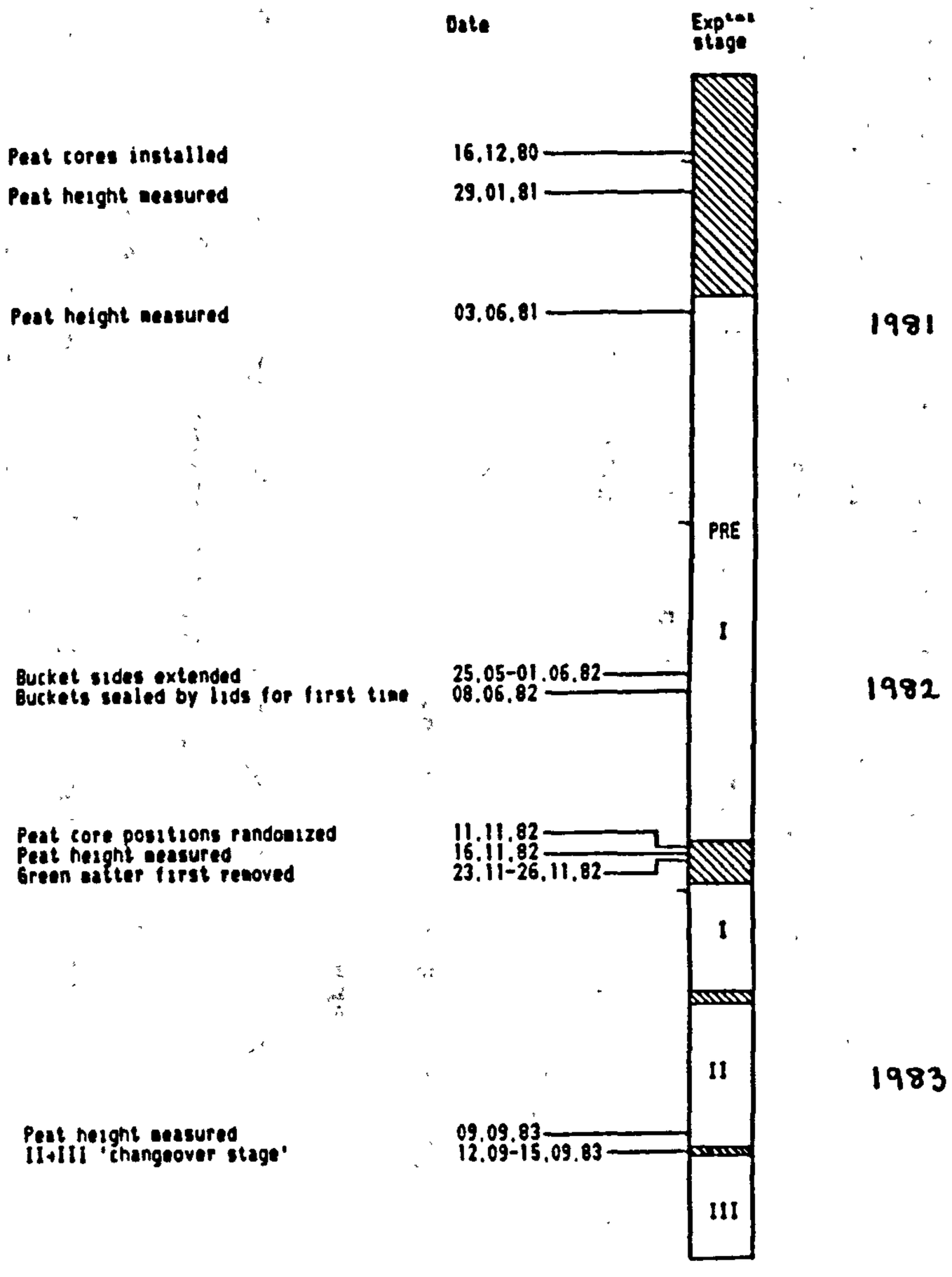
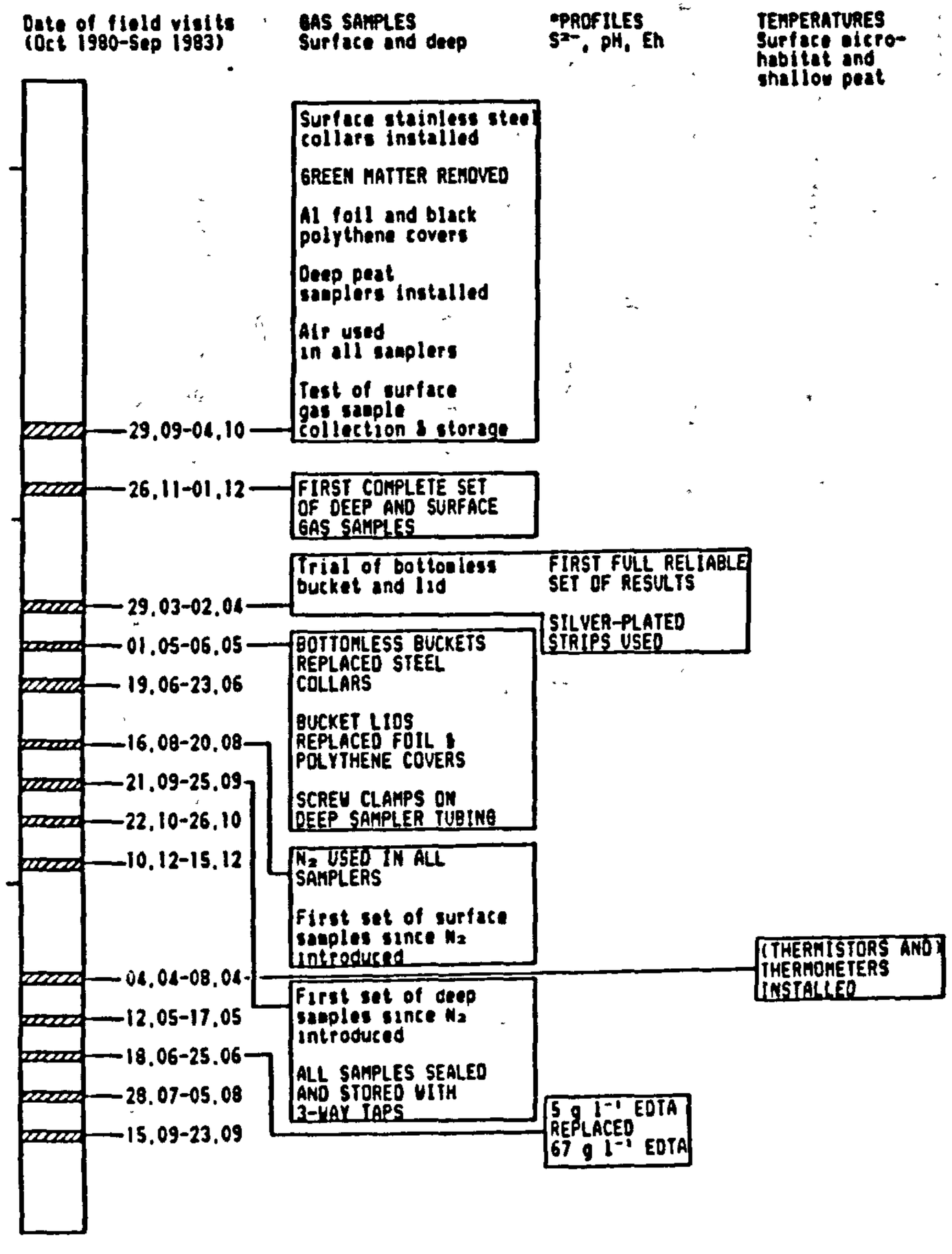


FIG. 4.1b. Installation and sampling chronology for field monitoring programmes. *Here 'Profiles' refers to top 30 cm sulphide zone records (silvered strips) and deep peat electrode measurements. CAPITALS indicate initiation of method which subsequently remained unchanged. Hatching indicates field visit.



occasion was it not possible to visit both Sites during a field trip; in December 1982 ice on the approach track prevented access to MH. The total depth of peat over which each set of surface samplers at a site was positioned, is given in Table 3.4, above (Section 3.3.3, Arrangement of Peat Gas Samplers).

In this 'Background' section, results of the weather monitoring are given first, followed by those of the laboratory peat gas diffusion experiments. Finally in this section, the water levels in the garden and field are reported. The second Results section describes surface gas flux, and the third, deep peat gas concentration profiles. The effect of removing the green matter is reported in the surface gas flux section. Profiles of pH, redox potential and total sulphide concentration are described in the final section of this chapter. Where possible, garden results are given first followed by the equivalent field results, for comparison.

4.1.2 WEATHER RECORD

The detailed results from the weather records made over the three years of the study, in the garden and in the field, are presented in Appendix G. The appendix also includes full details of methods, and results, of calculations to predict the change in temperature with depth and with season at the depth of the field gas samplers. The present account is a summary of the main features of the measurements and predictions.

SURFACE WEATHER PATTERNS

a) General

The mean air temperatures in the garden (+30 cm, 1230-1400h, $135 \leq n \leq 174$) for the three study years were 12.2°C (1981), 12.9°C (1982) and 12.0°C (1983) (Fig. 4.2), giving an overall annual mean air temperature for the garden of 12.4°C. Diurnal temperature changes were about 10-15°C in summer and 1-3°C in winter. The maximum temperature (around 25°C) occurred in July or August each year, and the minimum (about -2°C) between November and February.

FIG. 4.2 Garden air temperature, 1981-1983.
Weekly mean temperatures, Minibog 2, at + 30 cm.

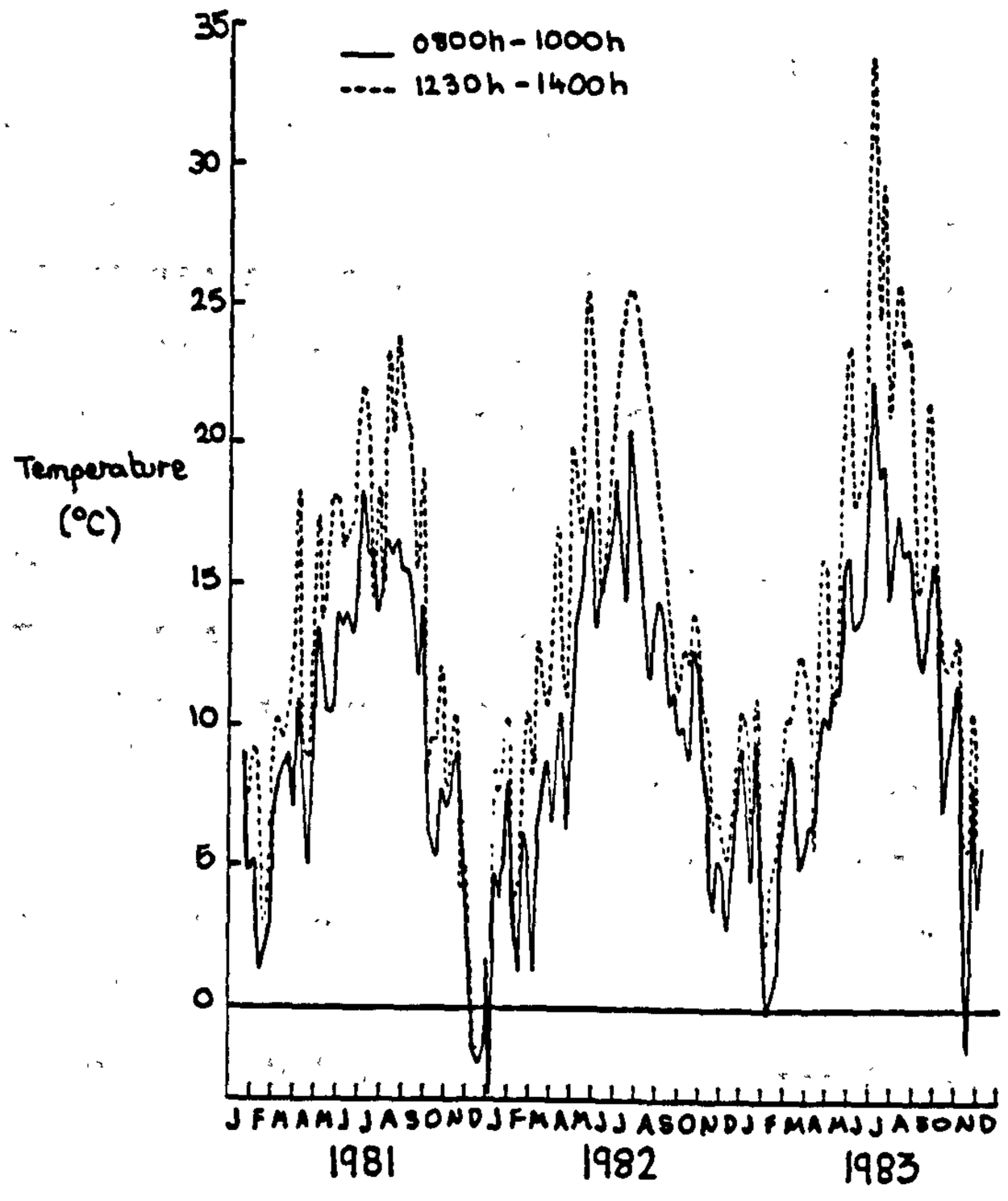
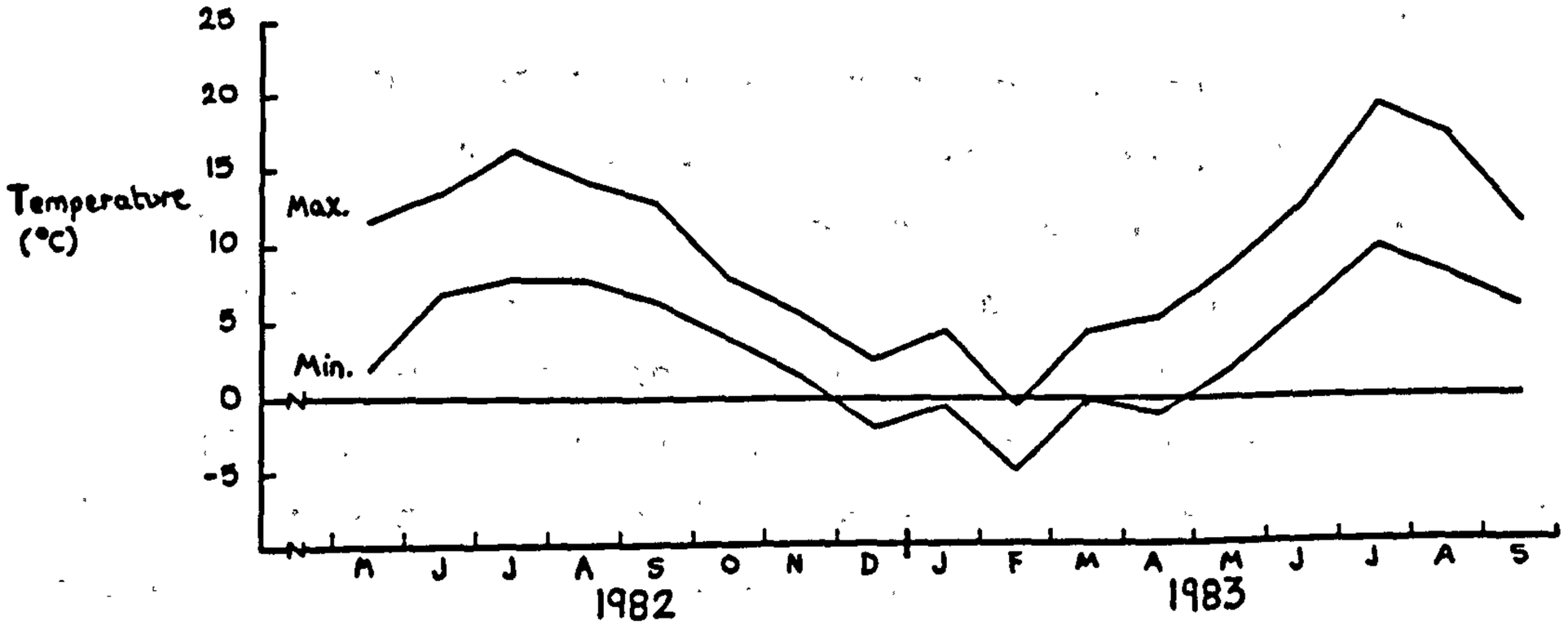


FIG. 4.3 Moor House air temperature, 1982-1983



Weather records for the field sites were made on each visit (results below), and to set these spot measurements in context and to allow a more reliable comparison between conditions in the field and those in the garden, Meteorological Office (Met. Off.) records for the MH area were obtained for the duration of the study period. The same records were used as an approximate description of conditions at CR, for which Met. Off. data are not available. Fig. 4.3 gives the Met. Off. monthly mean maximum and minimum temperatures recorded at Stevenson Screen height (+1.25 m), for the MH area. The values are estimates reached by using MH (altitude 558 m) and Widdybank Fell (about 7 km ESE of MH; altitude 513 m) data. The Fig. shows that 1983 was a warmer season at MH, as it was in the garden, but the temperatures were about 5-7°C lower, the maximum air temperature being 16°C in 1982 and 19°C in 1983; both occurring in July. The monthly minimum temperature remained above 6°C (roughly the limit for the growing season) between June and September (cf April to October in the garden). Minimum temperatures were recorded in December in 1981-2 (-7°C) and in February in 1982-3 (-5°C). The monthly minimum remained below 0°C between December and April in both winters (cf 1-4 weeks between November and February in the garden). The mean range of temperature was 8-10°C in summer, and about 5° or 6°C in winter. Thus the range is smaller at MH than in the garden by up to about 10°C, the largest difference occurring in the summer, and at MH there is less of a difference between the summer and winter ranges. The annual mean air temperature at MH, calculated as the 10-year mean from annual ½(max + min) values between 1961-70, was 4.9°C (Smith, undated). This appears a realistic value to use for the present study, on inspection of Fig. 4.3.

In the garden, ground frost (rime, frozen surface vegetation or pool water) was recorded between mid-October and March. At MH, there was no month of the year when ground frost did not occur (Met. Off. data). The number of days of frost recorded for each microhabitat showed almost no difference, except perhaps a tendency for pools to freeze slightly less often than either lawns or hummocks (Fig. G.2, p.449). Once frozen, the pools usually thawed more quickly than the hummocks, the lawns being intermediate in this respect. It was noted

TABLE 4.1 Surface weather summary for each stage of the garden experiment.

a) Temperature

Stage	Dates	Duration (weeks)	Mean daily air temperature at +30 cm 0830 h-1000 h (°C)	Mean daily air temperature at +30 cm 1230 h-1400 h (°C)	Mean daily temperature at 0 cm Max. (°C)	Mean daily temperature at 0 cm Min. (°C)	Range (°C)	Mean peat temperature at -30 cm Thermistor (°C)	Mean peat temperature at -30 cm Thermometer (°C)
PRE I	21.05.81 to 04.11.82	76	n=307 10.5 ±0.3	n=224 12.9 ±0.5	n=334 17.4 ±0.4	n=335 8.8 ±0.3	8.6	n=624 10.8 ±0.2	n=671 11.8 ±0.2
I	20.12.82 to 14.04.83	16	n=59 5.3 ±0.5	n=43 7.2 ±0.5	n=63 7.9 ±0.5	n=63 3.1 ±0.4	4.8	n=111 3.9 ±0.1	n=114 5.9 ±0.2
II	28.04.83 to 11.09.83	20	n=82 15.3 ±0.4	n=65 22.0 ±0.7	n=88 23.4 ±0.8	n=88 12.6 ±0.5	10.8	n=113 13.8 ±0.5	n=162 15.7 ±0.3
II-III CHANGE-OVER	12.09.83 to 15.09.83	4 days	n=4 12.6	n=3 13.7	n=4 16.5	n=4 11.9	4.6	?	n=7 14.4 ±0.2
III	26.09.83 to 14.12.83	11	n=38 7.6 ±0.8	n=25 10.7 ±1.0	n=41 11.9 ±1.0	n=41 4.8 ±0.8	7.1	?	n=73 10.2 ±0.3

? thermistor unreliable

b) Precipitation

Stage	Dates	Duration (weeks)	Total ppt^n (mm)	Mean total weekly ppt^n (mm)	Max. daily ppt^n (mm)	Date	No. rain days	No. frost days	No. snow days
PRE I	21.05.81 to 04.11.82	76	686	n=77 8.9 ±1.3	21	28.09.82	274	n=401† 31	n=401† 15
I	20.12.82 to 14.04.83	16	275	n=19 14.5 ±5.2	≈10	between 23.12.82 and 05.01.83	80	n=69† 16	n=69† 9
II	28.04.83 to 11.09.83	20	186	n=21 8.9 ±3.7	24	18.05.83	67	n=91† 0	n=91† 0
II-III CHANGE-OVER	12.09.83 to 15.09.83	4 days	17	n=4 4.1*	7	14.09.83	3	n=4† 0	n=9† 0
III	26.09.83 to 14.12.83	11	63	n=12 5.3 ±2.1	≈6	25.11.83 to 28.11.83	33	n=29† 12	n=29† 0

† No. records made * Mean daily ppt^n

on occasions that the hummocks were frozen to a depth of about 3 cm and if low daytime temperatures persisted they did not thaw completely during the day, although the surface *Sphagnum* did so. No cases of lawns remaining frozen for an entire day were noted.

During the study, snow in the garden was confined to February, except in 1981-82, when it was recorded between November and January. At MH snow was recorded (Met. Off.) on at least one day of each month between November and March.

Mean total annual precipitation in the garden for 1981-83 was 453 mm (including snow-melt), compared with 1938 mm (rainfall only) at MH. Rainfall was more evenly spread over the year at MH than in the garden. In 1981, the wettest March in 30 years was recorded in London. In the garden 57 mm of rain fell, compared with 25 mm and 19 mm in the following two years.

In all respects, 1981 was the coolest season of the study in the garden, with slightly lower summer temperatures and a longer season of frost in the ensuing winter. The 1981-82 winter also had more snow, and this occurred over a longer period. The 1983 field season was warmer and slightly wetter than that of 1982, but the mean minimum temperature remained below freezing for longer at the beginning of 1983 than in the previous year. Consequently, snow was slower to thaw in 1983 and persisted into April.

b) In relation to the garden experiment and field gas sampling

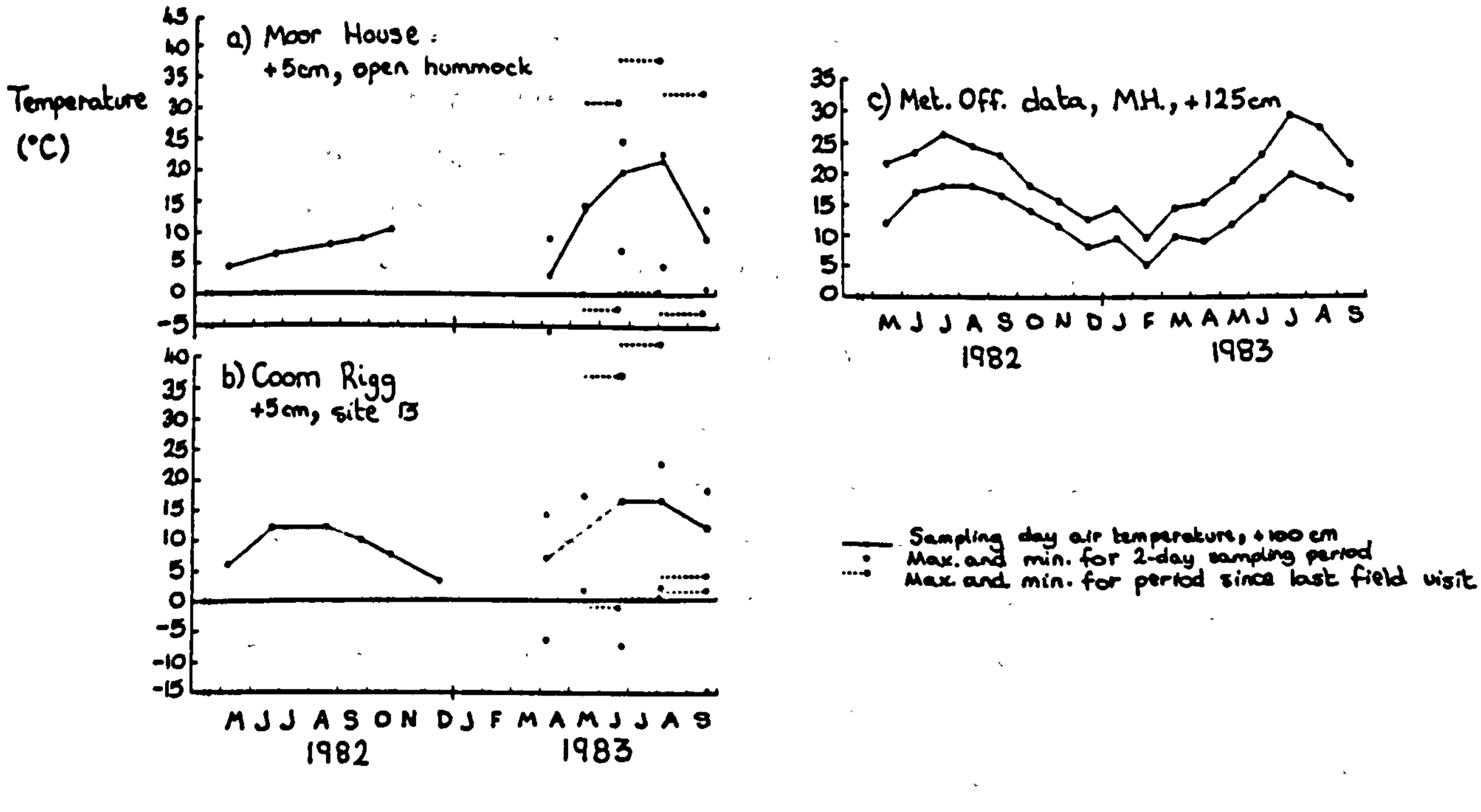
Table 4.1 summarises the surface weather records for the entire period of each stage of the garden experiment, including all periods between sampling days.

The mean temperature of the peat for the Pre I stage, as measured using the thermistor and including data from all months of the year, is insignificantly different from the mean morning air temperature, in accordance with the assumption that temperatures down a peat profile oscillate about a consistent annual mean value (see Appendix G). Unfortunately the thermistor readings became unreliable towards the end of stage II, but the Table shows that up to this point the thermometer readings were 1-2°C higher than those calculated by use of the thermistor. Using this to estimate the thermistor peat temperature gives results which further support the theoretical sine-

wave model of temperature fluctuations with depth (Appendix G): during most of the year as the surface temperature increases (stages I and II), the temperature at -30 cm in the peat is lower than the air temperature, but when the air temperature begins to fall markedly, from September onwards (stage III), the peat cools less rapidly and its temperature remains higher than that of the air. This effect is seen at least in the top 30 cm of peat.

Field Site air temperatures, recorded on each field visit, are shown in Figs. 4.4a and b. Maximum and minimum temperature data are available from April 1983 only. Fig. 4.4c reproduces the Met. Off. records shown in Fig. 4.3, for comparison. The temperature records

FIG. 4.4 Air temperatures measured during field visits



made on field visits reflected the Met. Off. data accurately, except in the case of the MH 1982 data, which showed a continued increase in air temperature from May to October. The Met. Off. data provide important information on temperature changes between sampling dates and maximum and minimum data where these are otherwise lacking. For example, the severe drop in temperature in February 1983 was too early

to be recorded on a field visit, but could have important effects on the onset of significant microbial activity and gas production for that year.

Gas samples were collected at times which represent a range of air temperatures between 3°C and 22°C. For the same periods, the monthly mean maximum and minimum temperatures recorded between successive field visits are shown in Fig. 4.4. The gas samples representing the gas flux at the coldest time sampled were collected on the first trip of each year (May 1982 and April 1983), except at CR in 1982 where the December visit had the lowest temperature of all visits that year. However, after a summer of higher temperatures the peat will have been warmed, so that these fluxes are not directly comparable with those at the beginning of the field season. Except for the MH 1982 samples, June and August samples represented those from the warmest (air temperature) period of the year, both in terms of the spot air temperature and the Met. Off. data. From Fig. G.7 (p.452) it can be seen that most field gas samples were collected in the drier months of the year, with the exception of December 1982 at CR. Samples in August, September and October 1982 and September samples in 1983 represent months with intermediate rainfall:

c) The effect of the bucket on internal air temperature

At intervals during the study the air temperature inside and outside sealed peat buckets was measured, both in the garden and in the field. A total of 72 such pairs of measurements were made (Fig. 4.5), spanning a temperature range of -5°C to 25°C. The largest difference between internal and external temperatures was 4.5°C, but this was extreme; the mean difference was 0.24°C and a paired t-test yielded a non-significant value of t (0.75) at the 5% level of significance.

PEAT TEMPERATURE

a) Changes with microhabitat and depth (measured)

Fig. 4.6 shows the temperature of the peat (thermistor readings) at about -20 cm to -30 cm in the garden peat cores P1 (pool), L1 (lawn) and H1 (hummock), and the corresponding garden air temperature

FIG. 4.5 Air temperatures inside and outside sealed peat buckets

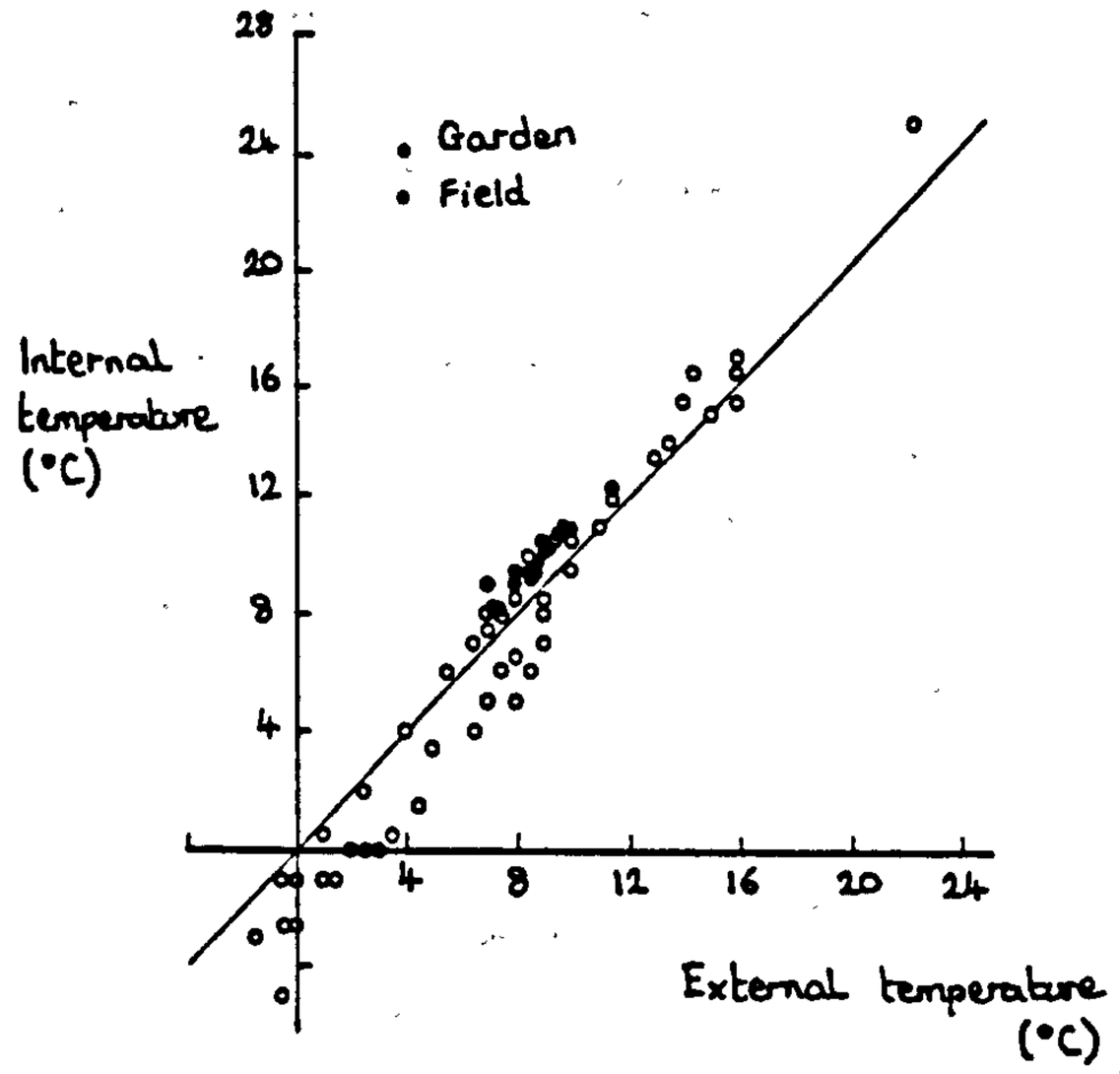
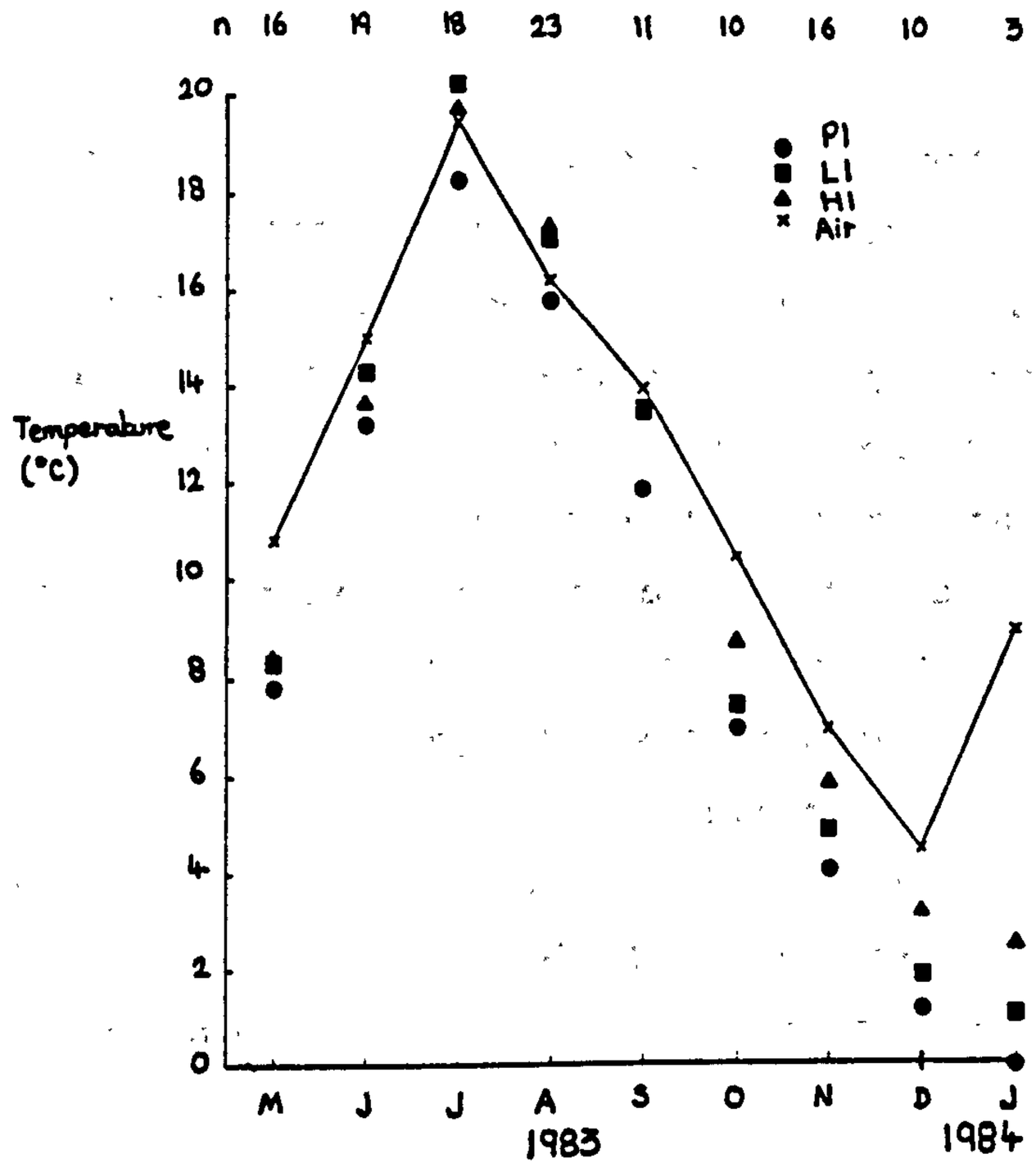
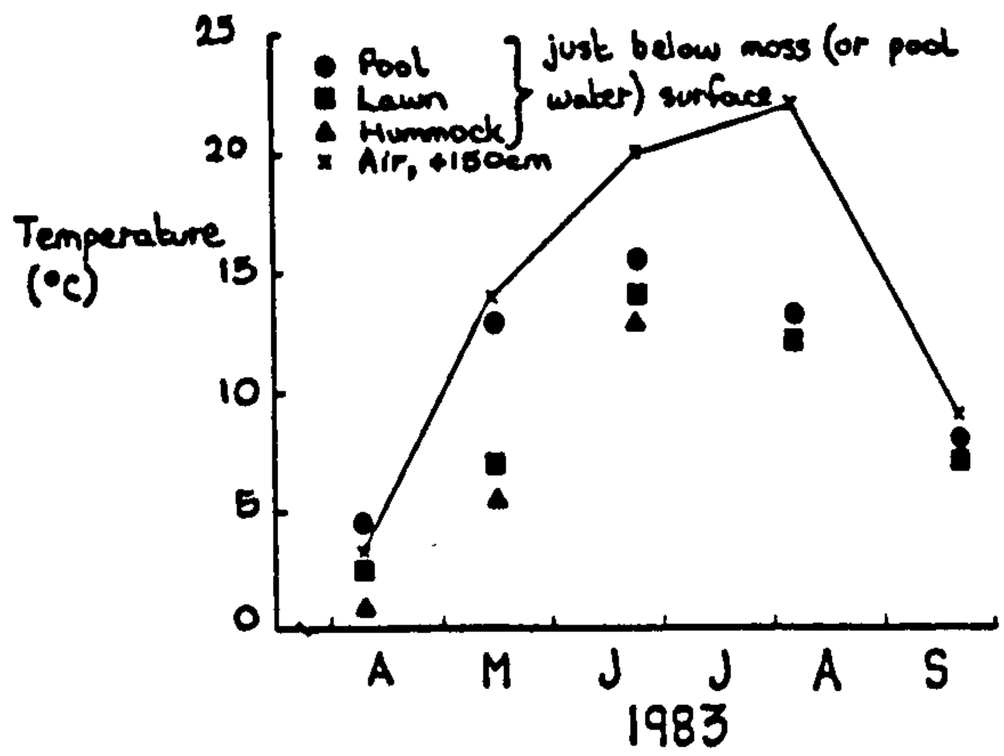


FIG. 4.6 Pool, lawn and hummock peat temperature in garden plot. Temperature at -20 cm to -30 cm. Means of n readings, 0800h-1000h. Mean monthly air temperature (+30 cm), for comparison.



(+30 cm), for the period May 1983 to January 1984. At MH in 1983 the temperature of pools, lawns and hummocks was recorded when the gas samples were collected (usually at about mid-day), 5 cm below the moss layer (or water surface in the case of pools). The results are plotted in Fig. 4.7, and compared with the corresponding air temperature (at +1.5 m). Both Figures show, on the whole, a lower peat temperature than that of the air and a difference in peat temperature between the microhabitats down to at least -30 cm. However, the results from the garden and the field differ in detail.

FIG. 4.7 Pool, lawn and hummock peat temperature at Moor House. Measured at sampling.



In the garden, the peat temperature at about -30 cm was around that of the air temperature at +30 cm in the hottest months of the year, but was up to 29°C lower at colder times, depending on the microhabitat. Conversely, in the field it appeared that the peat temperature (-5 cm) was most similar to that of the air at the cooler times of the year, and was up to 10°C cooler in the summer.

Of the three microhabitats, pools consistently showed the lowest peat temperature in the garden cores but the highest in the field. Neither was there consistency in the relative temperature of lawns and hummocks, except that in the garden and the field lawns were one or two degrees warmer than hummocks as long as the air temperature increased. As the air temperature fell after the summer peak, garden hummock temperature fell less quickly than that of lawns so that their

absolute temperature was the higher of the two. In the field, there was no difference in the temperature between the two during this period.

Thus it is clear that in general the temperature of the peat, at least to -30 cm depth, is lower than that of the air, and that there are differences in peat temperature between microhabitats at these shallow depths. The precise nature of the differences are not consistent, however, and are likely to be an integrated manifestation of complex interactions between many factors such as surface windspeed, shading and thermal capacity and conductivity of the peat itself, which each depend on their own specific set of variables.

FIG. 4.8 Comparison of peat temperature at two Coom Rigg sampling sites

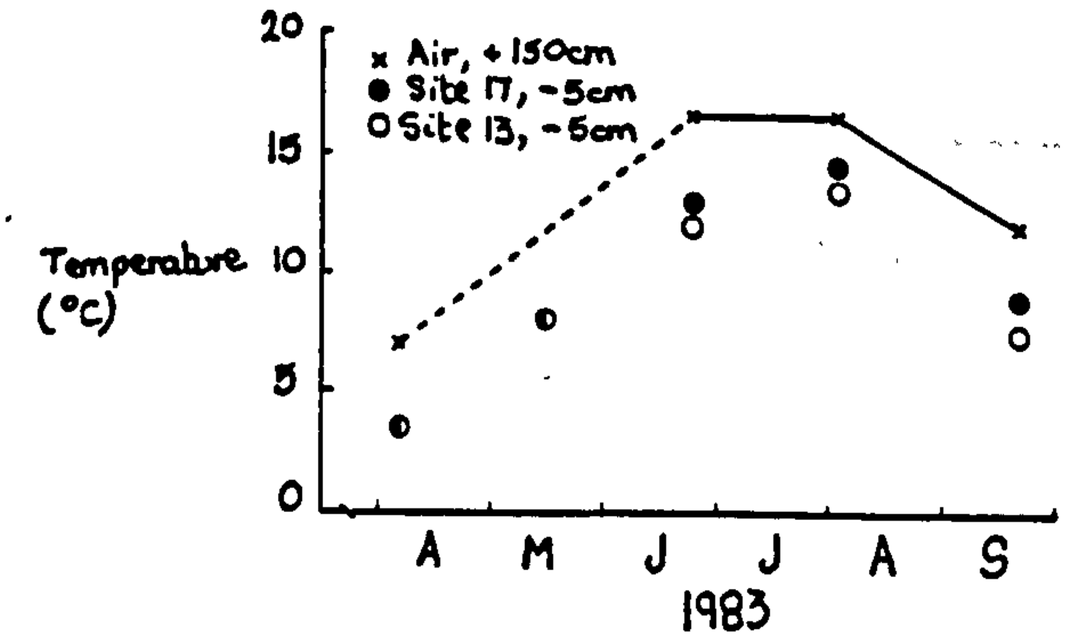
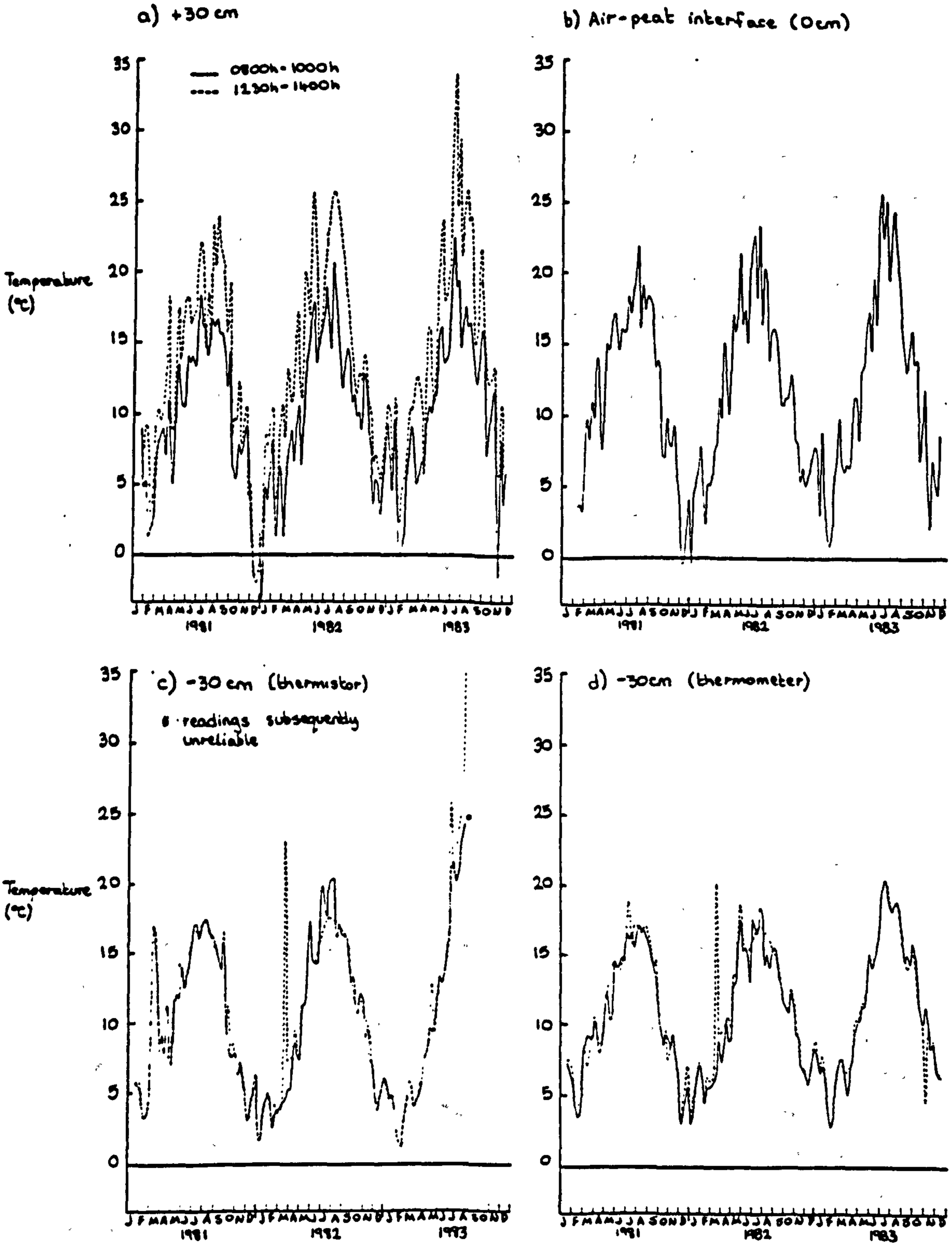


Fig. 4.8 shows a comparison between the peat temperature 5 cm below the moss surface at the time gas samples were collected, for sites 13 and 17 at CR. Site 13 was situated well out on the bog while site 17 was located in the lagg, adjacent to the conifer (*Picea sitchensis*) plantation margin (see Fig. 2.5). Early in the season (April and May records) the temperatures coincided, but thereafter site 17 was between one and two degrees warmer than site 13. This presumably results from the greater degree of protection from the wind afforded by the conifers, an effect which was evident at a depth of at least 5 cm. From this, it is reasonable to assume that differences in the annual temperature régime between sites 13 and 17, potentially the

FIG. 4.9 Comparison of temperature at three points in the Minibog 2 air-peat column



two most extreme sites at CR in this respect, will not be more than those recorded between the different microhabitats at MH.

It is convenient to note here that on no field visit was the peat frozen below the surface.

Peat temperatures at -30 cm in minibog M2 were recorded simultaneously using a thermometer and a temperature-calibrated thermistor. Unless stated otherwise, in the subsequent Results sections the thermistor records are used except where these are erratic, in which case the predicted thermistor temperature is calculated using the appropriate regression equation (see Appendix G).

Fig. 4.9 shows the weekly mean temperatures for M2 at -30 cm depth (thermistor and thermometer results), and at the air-peat interface. The air temperature 30 cm above M2 is reproduced here from Fig. 4.2 to facilitate comparison.

The graphs illustrate several important points about the temperature regimes at various points in an air-peat column:

At a depth of -30 cm

i) the difference in morning and afternoon temperatures is negligible compared to that recorded 30 cm above the surface,

ii) the peat temperature is roughly equal to the morning air temperature and remains lower than the afternoon air temperature,

iii) the amplitude of the high-frequency fluctuations is smaller than those of the air temperature above, and

iv) the amplitude of the annual temperature changes is smaller than that in the air above; summer temperatures are lower and winter temperatures higher.

At the air-peat interface temperature conditions are intermediate between air and peat regimes.

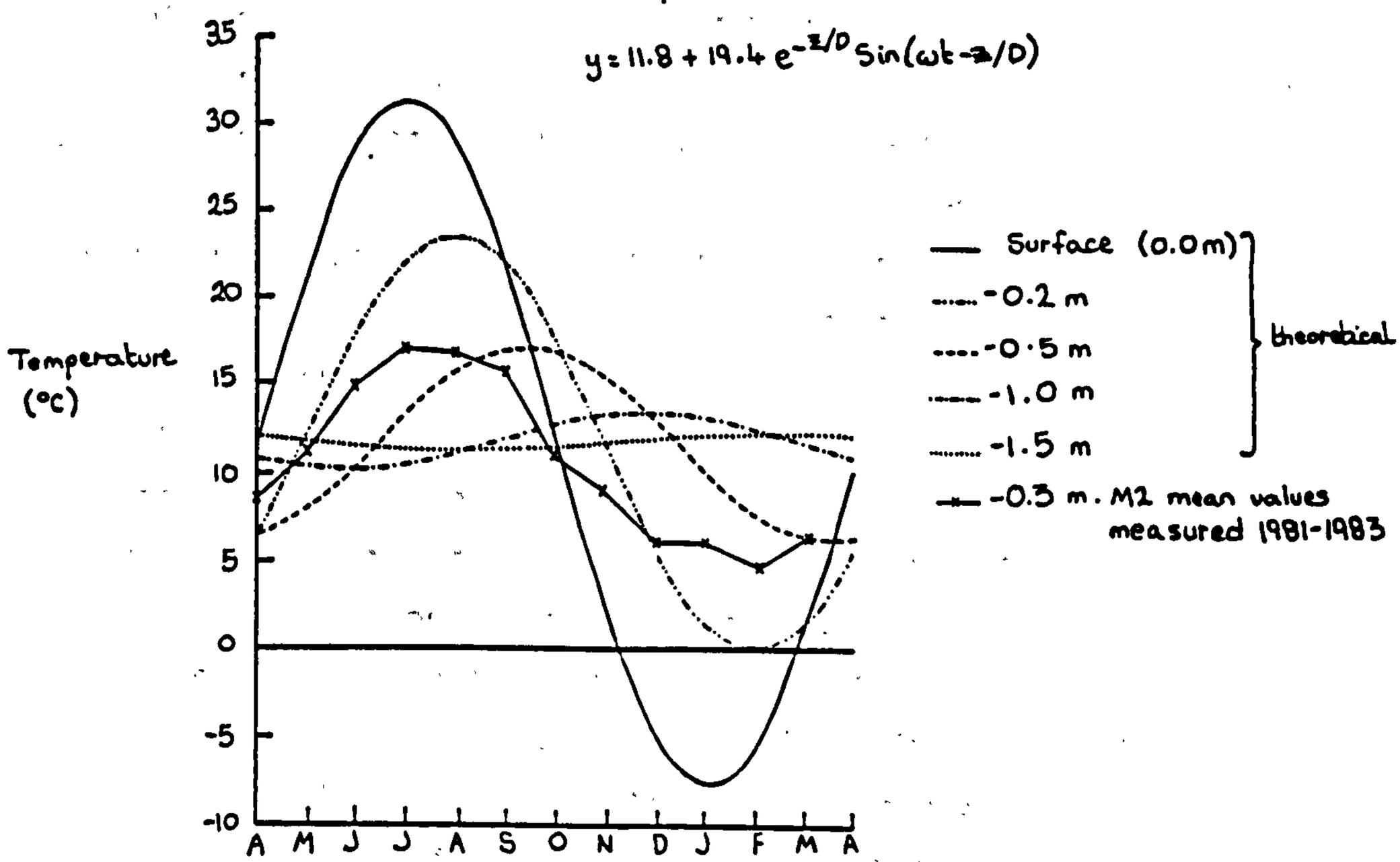
b) Changes with depth (predicted)

The thermistors which were installed in the field peat gave unreliable results in the main, so insufficient data were collected to enable a description of the seasonal temperature changes down the peat profile to be made. However, theoretical predictions are possible using the data available, and these yield useful information concerning heat flow through the peat. The details of the calculations and the full set of results are given in Appendix G.

The equation used to model the annual and daily (sinusoidal) temperature oscillations in the peat predicts that as depth increases, the amplitude of the oscillations is reduced, and that there is a shift in the position of the maxima and minima relative to those at the surface. At the damping depth, D, the amplitude of the surface oscillations is reduced to e^{-1}, or 0.37x, that at the surface. The quantity D is specific for different cycle lengths, and is dependent on the thermal properties of the medium. It can be calculated from temperature data such as have been collected in the present study, and can then be used to estimate other parameters which approximately describe heat movement through the peat.

Using different data sets collected during the present study or taken from the literature, a number of estimates of D were made (Table G.1, p.456) which suggested that the annual damping depth, D_a, for the blanket peat under consideration was between about 40 cm and 80 cm. Once an estimate of D is available, it can be substituted into the model to generate predictive temperature oscillations for the peat. This was done for each depth at which a field gas sampler had been placed, down as far as the maximum depth of the M2 minibog. The results are shown in Fig. 4.10, and the *measured* temperatures for M2 are plotted for comparison. The predicted values appear reliable. Three such plots were produced; that reproduced in Fig. 4.10 was based on air and peat temperature measurements made in M2 for the present study, a second was based on the value of D_a estimated from M2 data and measured air temperature data from MH, and the third on a value of D_a and air temperatures obtained using 1981 records from the ex-Met. Off. station at MH. The complete series of plots is given in Appendix G. They each illustrate the damping effect and the phase shift of the surface oscillations with increasing depth. The temperatures at all depths fluctuate around the annual mean air temperature: 5°C for the plots based on MH data, and 12°C for those based on M2 data. Indeed, a comparison of the field and garden plots show that maximum and minimum temperatures at all depths in the garden peat are elevated compared with those at the same depths in the field; the temperature ranges are similar.

FIG. 4.10 Measured and theoretical annual temperature oscillations in Minibog 2. For further explanation of calculations, see App. G.



The smaller surface amplitude figure used in the predictive plots shown in Fig. G.9 (p.461) results in smaller absolute temperature changes down the peat profile than at the same depth in the other cases, despite the 80 cm damping depth compared to 40 cm used for the others. Thus the value of the damping depth is important when relating temperatures and their possible effects down a profile, but the surface temperature range and the consequent absolute temperature changes at depth must be borne in mind when assessing the significance of these changes.

The effective depth for heat flow, as given mathematically by the expression $G_D = 2^{0.5}D$, is ≈60 cm or ≈110 cm depending on which value of D is used, and is clearly seen from the graphs. At depths below these the annual temperature range is negligible, being, at most, about 3°C.

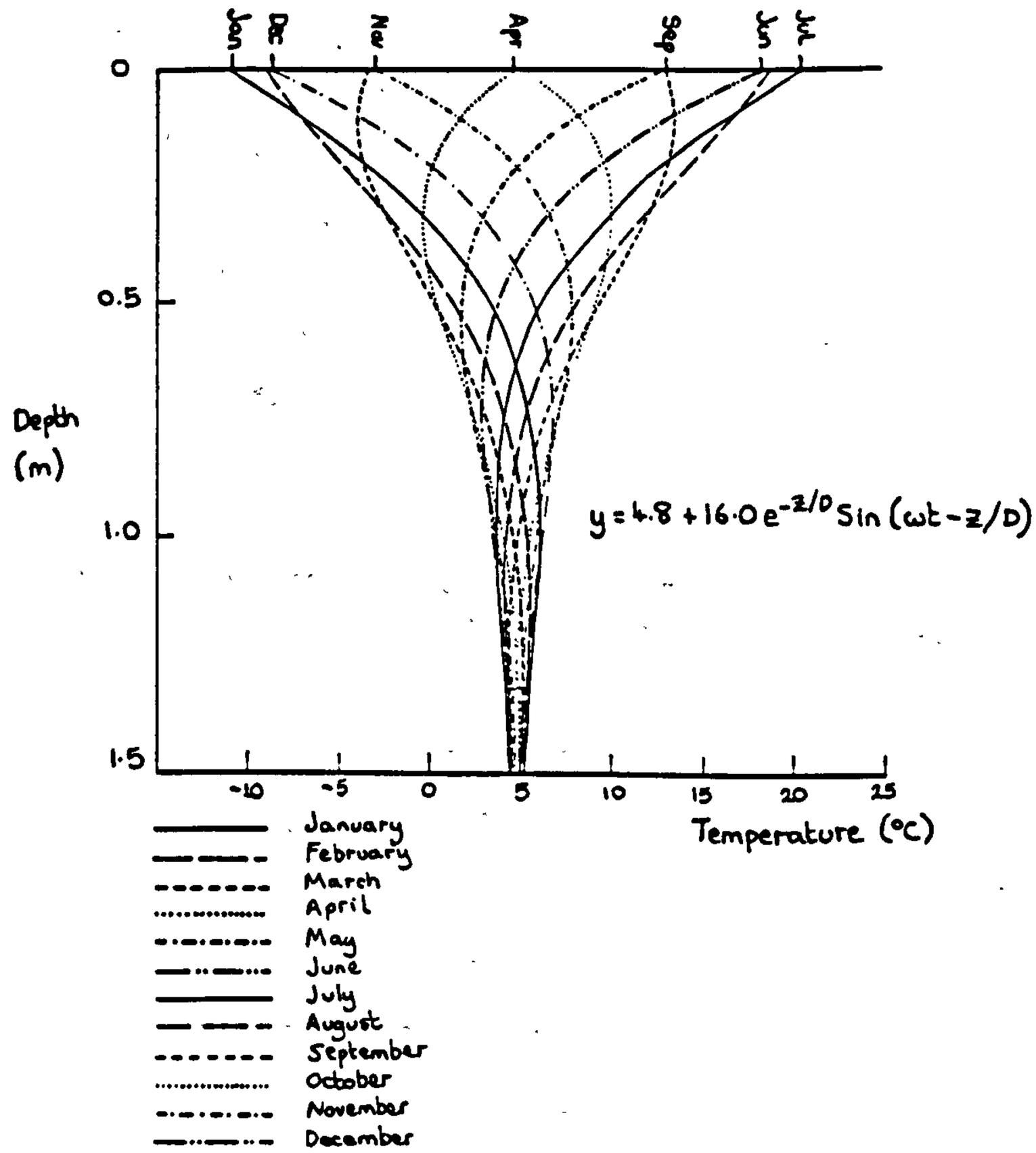
There is a time lag between the occurrence of the maximum temperature (or any other point on the wave) at the surface and at any point in the profile. It appears from the plots that the maximum

temperature at -20 cm occurs about a month behind that at the surface (and is damped) and that it takes about 10 weeks to reach -50 cm. The oscillations become negligible at about -1 m, or slightly less. The depth, z, at which the annual oscillations in the peat are exactly out of phase with those at the surface, may be calculated from the expression $z = \pi D_d$, and evaluates to -1.5 m or more, depending on the data set used. At these depths, however, the amplitude of the oscillations will be negligible.

Although it was not possible to be certain of the annual damping depth, in practice the exact value is not critical, since whether it is closer to 40 cm or 80 cm the results from the samplers at -50 cm are likely to be subjected to significant temperature fluctuations whereas those at -100 cm are not. The true value is probably somewhere between the two. In the middle of the year (April to September) the peat body is cooler than the surface and above, whereas after the warming effect of the high summer temperatures the converse is true (October to March). This is illustrated in Fig. 4.11, which is an enlargement of the top 1.5 m portion of Fig. G.9bii (p.461), and shows the predicted temperature profiles on the first day of each month, based on data set b) in the appendix. Hence, samplers buried at depths of up to about 60 cm will be subjected to increasingly cool conditions with depth in the middle of the year, but those closer to the surface will be warmed from below at the end of the year, and more quickly from above when surface temperatures rise above those of the peat.

Estimates of the daily damping depth, D_d, were made for each of the three microhabitats separately, since the difference between the three in water content of the shallowest regions of the profile might be expected to have an effect. Again, the details of the field data used, and the full set of results, are included in Appendix G, but D_d appeared to be less than 5 cm, and to increase with the wetness of the habitat. This in accordance with the measured peat temperatures at MH (Fig. 4.7). The daily damping depths, based on field data for sites 13 and 17 (collected between April and September 1983), were also estimated. Here, too, there was a suggestion that D_d was deeper at

FIG. 4.11 Theoretical peat temperature profiles over the top 1.5 m, Moor House (annual cycle)



the wetter site (13), though the absolute difference was less than 1 cm.

4.1.3 GAS DIFFUSION RATES THROUGH PEAT

Six experiments were set up to measure the diffusion rate of methane and carbon dioxide through field peat (see Section 3.1.3, Measurement of Gas Diffusion Rates Through Peat).

For the subsequent calculations of diffusion rate to be valid, certain conditions must be satisfied, as described in Appendix E). In

practice the conditions proved difficult to achieve, and of the 36 potential data sets (6 experiments x 3 tubes x 2 components) only 7 were useable by those criteria. In the first experiment the concentration of CH_4 and CO_2 in end B relative to that in end A increased above acceptable levels, and the experiment was not carried out at constant temperature. The main problem in the other cases was that despite having increased the concentration gradient dramatically at the beginning of stage 2 compared with that in stage 1 (= 0 vpm cm^{-1}), there was no corresponding (significant) increase in the mean concentration of components in end B during stage 2. In some cases the concentrations in end B decreased slightly, though this was seen almost exclusively for CO_2.

FIG. 4.12 Changes in CH_4 and CO_2 concentration during Experiment 2 to determine the rate of diffusion of gases through peat

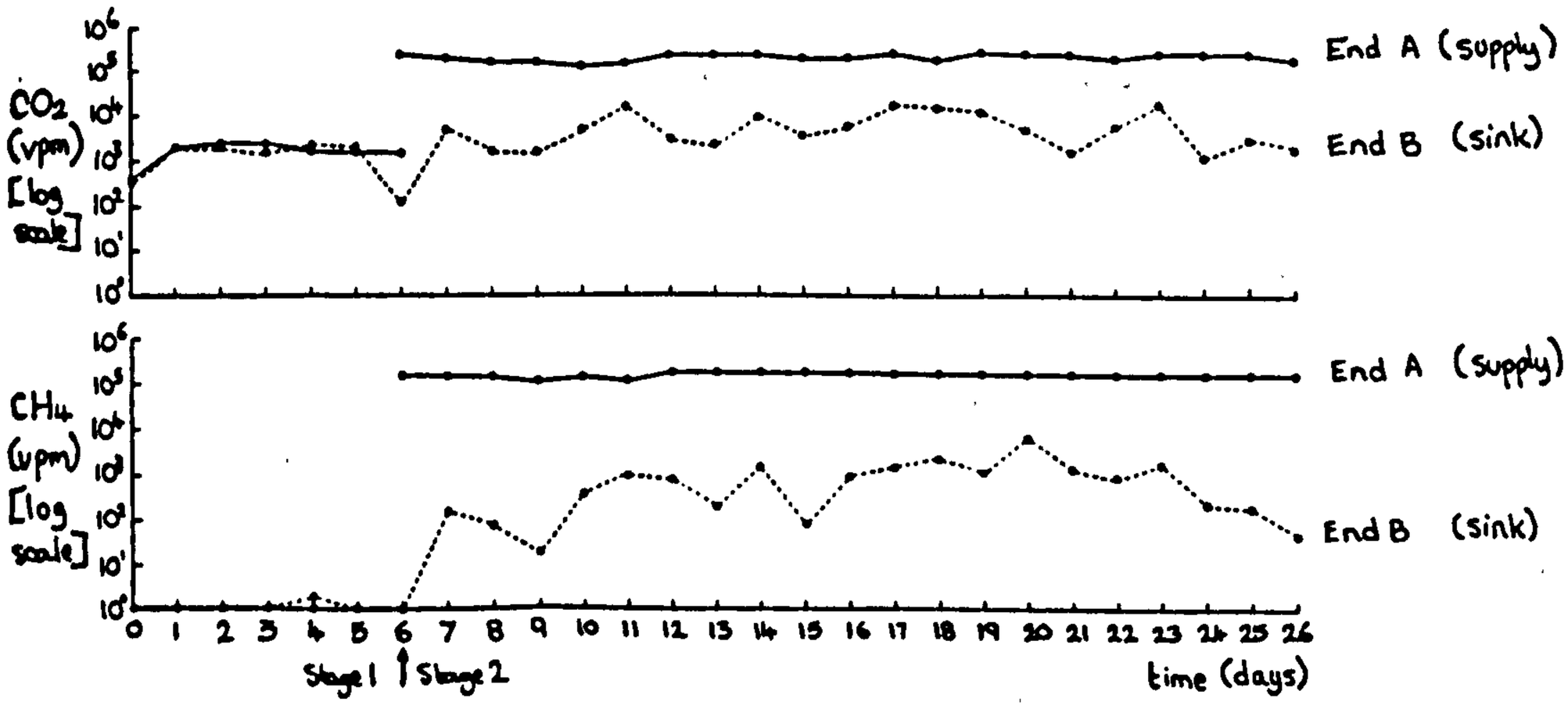


Fig. 4.12 shows the changes in concentration of CH_4 and CO_2 in tube 2 during Experiment 2. Table 4.2 gives the results of calculations with the seven useable data sets. Details of the method, and an example, are given in Appendix H.

The range of values for the CH_4 diffusion coefficient in peat according to Table 4.2 is large, from 1-271 $cm^2\ y^{-1}$ (4 x 10^{-9} to 8.6 x 10^{-6} $cm^2\ s^{-1}$). There is no correspondence between bulk density or the depth from which the core was collected and the diffusion rate.

TABLE 4.2 Summary of results from experiments to determine gas diffusion rates through peat. Calculated for peat of the specified bulk density, at 20°C, with the given concentration gradient. Details of the calculations are shown in Appendix H.

a)

Expt	Tube	Gas	Mean Concn end B, Stage 1 (B_1) ($\mu g cm^{-3}$)	Mean Concn end B, Stage 2 (B_2) ($\mu g cm^{-3}$)	Mean Concn change (B_2-B_1)†1 ($\mu g cm^{-3}$)	Volume end B (cm^3)	Mean Mass change, end B dm†2 (μg)	Mean Concn end A, Stage 2 dc†3 ($\mu g cm^{-3}$)
2	2	CH_4	$8,16 \times 10^{-4}$	0,897736	0,89692	427	382,98	143,642
2	3	CH_4	$4,71 \times 10^{-4}$	0,097659	0,09719	553	53,745	138,521
2	3	CO_2	4,36	10,405422	6,044422	553	3342,565	437,472
3	2	CH_4	$8,39 \times 10^{-3}$	0,0141372	$5,7477 \times 10^{-3}$	352	2,023190	161,664
5	1	CH_4	0,01438	0,195398	0,181018	528	95,5775	248,897
5	2	CH_4	0,41004	0,4683	0,05826	352	20,508	248,1422
5	3	CH_4	0,01581	0,130032	0,114222	478	54,598	239,0676

b)

Expt	Tube	Gas	Core length dl (cm)	Concn grad. (dc/dl) ($\mu g cm^{-3} cm^{-1}$)	Bulk density (ρ) ($g cm^{-3}$)	Diffusion coefficient (D_h) ($cm^2 h^{-1}$)	Diffusion coefficient (D_s) ($cm^2\ s^{-1}$)	Diffusion coefficient (D_y) ($cm^2\ y^{-1}$)
2	2	CH_4	14,0	10,26	0,13	0,031	$8,6 \times 10^{-6}$	271
2	3	CH_4	6,0	23,09	0,18	$1,9 \times 10^{-3}$	$5,4 \times 10^{-7}$	17
2	3	CO_2	6,0	72,91	0,18	0,038	$1,1 \times 10^{-5}$	333
3	2	CH_4	14,0	11,55	0,096	$1,45 \times 10^{-4}$	$4,04 \times 10^{-8}$	1
5	1	CH_4	8,0	31,11	0,065	$2,5 \times 10^{-3}$	$6,9 \times 10^{-7}$	22
5	2	CH_4	14,0	17,72	0,096	$9,6 \times 10^{-4}$	$2,7 \times 10^{-7}$	8
5	3	CH_4	9,5	25,17	0,052	$1,8 \times 10^{-3}$	$5,0 \times 10^{-7}$	16

Notes

†1. Mean concentration change between Stage 1 and Stage 2 end B results i.e. concentration change per sampling period in end B due to introduced concentration gradient. Baseline subtracted.

†2. Mean mass change, end B = [mean concentration change (B_2-B_1)] x volume end B.

†3. Strictly, dc is the mean concentration difference between ends A and B in Stage 2, i.e. the change in concentration across the core. Since the concentration in B is taken to be zero, $dc \approx$ concentration in end A, Stage 2. Concentration in B taken as zero because it starts as zero and is never >2% that in A at maximum (end of sampling period).

Diffusion rates for gases in water given in tables are usually of the order of 10^{-6} $cm^2\ s^{-1}$; the values calculated here are generally within an order of magnitude of these, but are lower.

Only one data set for CO_2 could be used, and this gave a diffusion coefficient of 333 $cm^2\ y^{-1}$ (1.1×10^{-6} $cm^2\ s^{-1}$). This is surprising, since it would be expected that CO_2 diffused more slowly

than CH_4 under the same conditions (experiment 2, tube 3) (Graham's Law). Considered in retrospect, it is possible that introduction of (high concentrations of) CO_2 to the cores may have upset the usual position of any equilibrium between aerobic and anaerobic metabolism in the peat, providing a source of oxygen which could be utilised as it diffused through the core, and resulting in a reduction in the rate of methane formation, as well as a drop in CO_2 concentration in some cases. It is possible, too, that more refined experimental methods would yield more conclusive (and reliable) results. As already mentioned, the experiments were difficult to set up and to monitor. The manipulations involving water to displace the gases in the tube ends after each sampling may be partly responsible for inconsistency in the results, since they would involve some small pressure changes and possibly variation in pore water content at the ends of the cores.

4.1.4 WATER LEVEL REGIMES

All water levels are reported as depth relative to the peat surface, i.e. a positive value represents standing water.

GARDEN

The water level in each garden peat core was kept at a given (nominal) depth below the peat surface throughout each stage stage of the garden experiment. Water levels were changed at the end of each stage and were left for a few days to settle before the next stage began. Surface gas flux and the position of the sulphide zone were monitored during each stage. The experimental design of the water level regulation is shown in Table 4.3 ('required level').

The duration of each stage is shown in Fig. 4.1a and Table 4.1. Regular monitoring of the regulated water levels began in April 1981 and the Pre I stage of the garden experiment began with the first gas flux measurements, on 21 May 1981. The Pre I stage was divided into two separate phases. The first of these was concerned with determining the correct methodology for gas sampling; and samples were taken from cores P1, L1 and H1 only, using a cover of black polythene

TABLE 4.3 Garden water levels - Required and achieved.
Water levels (cm, *below* peat surface), assuming no growth between peat measurements

Treatment Stage	Date	H1	Pools	Lawns	Hummocks
PRE I[1]	21.05.81 to 07.06.82		0 0,8 ±0,5 Controls 4 17 | 0 −0,1 ±0,3 7 50	3 3,6 ±0,3 Controls 4 36 | 3 4,8 ±0,4 8 38	10 10,4 ±0,3 Controls 4 35 | 10 10,2 ±0,4 8 35
PRE II[2]	08.06.82 to 22.11.82	3,8 ±0,8 17	0 1,8 ±0,8 Controls 4 8 | 0 0,7 ±0,6 7 18	3 4,4 ±2,2 Controls 4 12 | 3 9,1 ±1,9 8 15	10 11,3 ±2,3 Controls 4 12 | 40 10,2 ±1,0 8 16
PRE III[3]	27.11.82 to 16.12.82		Uncut pools: 0 4,6 ±0,7 Controls 2 4 | 0 4,4 ±2,0 3 6; P5 P11 | P4 P8 P10. Cut pools: 0 3,6 ±0,4 Controls 2 4 | 0 0,5 ±0,6 4 8; P7 P9 | P1 P2 P3 P6	Uncut lawns: 3 3,3 ±0,3 Controls 2 4 | 3 4,7 ±1,0 4 8; L1 L12 | L2 L3 L4 L8. Cut lawns: 3 9,9 ±1,7 Controls 2 4 | 3 7,5 ±1,1 4 8; L6 L11 | L5 L7 L9 L10	Uncut hummocks: 10 9,9 ±0,2 Controls 2 4 | 10 9,6 ±0,3 4 8; H1 H12 | H5 H7 H10 H11. Cut hummocks: 10 11,8 ±1,8 Controls 2 4 | 10 9,7 ±0,2 4 8; H3 H8 | H2 H4 H6 H9
I	20.12.82 to 14.04.83	3,3 ±1,7 4	Uncut pools: 0 5,0 ±0,3 Controls 2 30 | 0 3,9 ±0,0 3 45; P5 P11 | P4 P8 P10. Cut pools: 0 3,5 ±0,1 Controls 2 30 | 0 −0,2 ±0,3 4 60; P7 P9 | P1 P2 P3 P6	Uncut lawns: 3 3,0 ±0,1 Controls 2 30 | 3 4,2 ±0,3 4 60; L1 L12 | L2 L3 L4 L8. Cut lawns: 3 9,2 ±0,3 Controls 2 30 | 3 5,9 ±0,3 4 60; L6 L11 | L5 L7 L9 L10	Uncut hummocks: 10 9,6 ±0,2 Controls 2 30 | 10 10,0 ±0,1 4 60; H1 H12 | H5 H7 H10 H11. Cut hummocks: 10 10,4 ±0,1 Controls 2 30 | 10 10,3 ±0,1 4 60; H3 H9 | H2 H4 H6 H9
II	28.04.83 to 09.09.83	5,8 ±5,9 3	Uncut pools: 0 4,5 ±0,2 Controls 2 26 | 5 9,4 ±0,8 ↓5 3 39; P5 P11 | P4 P8 P10. Cut pools: 0 4,9 ±0,5 Controls 2 26 | 5 5,5 ±0,5 ↓5 4 53; P7 P9 | P1 P2 P3 P6	Uncut lawns: 3 3,9 ±0,3 Controls 2 26 | 8 11,2 ±0,5 ↓5 4 52; L1 L12 | L2 L3 L4 L8. Cut lawns: 3 9,6 ±0,4 Controls 2 26 | 8 11,4 ±0,4 ↓5 4 52; L6 L11 | L5 L7 L9 L10	Uncut hummocks: 10 11,0 ±0,4 Controls 2 26 | 15 16,9 ±0,5 ↓5 2 26 | 5 5,6 ±0,2 ↑5 2 26; H1 H12 | H5 H7 | H10 H11. Cut hummocks: 10 12,1 ±0,7 Controls 2 26 | 15 16,3 ±0,3 ↓5 2 25 | 5 8,0 ±0,3 ↑5 2 25; H3 H8 | H2 H4 | H6 H9
III	26.09.83 to 14.12.83	17,8 ±3,9 5	Uncut pools: 0 4,7 ±0,5 Controls 2 16 | 10 14,4 ±0,9 ↓5 3 24; P5 P11 | P4 P8 P10. Cut pools: 0 4,2 ±0,1 Controls 2 16 | 10 7,5 ±0,6 ↓5 4 32; P7 P9 | P1 P2 P3 P6	Uncut lawns: 3 3,7 ±0,1 Controls 2 16 | 13 19,0 ±0,7 ↓5 4 32; L1 L12 | L2 L3 L4 L8. Cut lawns: 3 9,4 ±0,4 Controls 2 16 | 13 18,8 ±0,5 ↓5 4 32; L6 L11 | L5 L7 L9 L10	Uncut hummocks: 10 11,0 ±0,2 Controls 2 16 | 5 7,2 ±0,3 ↑10 2 16 | 10 11,1 ±0,2 ↓5 2 16; H1 H12 | H5 H7 | H10 H11. Cut hummocks: 10 10,6 ±0,1 Controls 2 16 | 10 11,7 ±0,4 ↑5 2 16 | 15 17,9 ±0,2 ↓10 2 16; H3 H8 | H2 H4 | H6 H9
PRE II to III	21.05.81 to 14.12.83	6,2 ±1,3 29	0 4,0 ±0,2 Controls 4 171	3 5,9 ±0,2 Controls 4 169	10 10,7 ±0,2 Controls 4 170
I to III	20.12.82 to 14.12.83	10,0 ±2,8 12	0 4,5 ±0,1 Controls 4 144	3 6,4 ±0,3 Controls 4 114	10 10,5 ±0,1 Controls 4 114

Notes

1. Polythene and foil covers; before vegetation removed
2. Lids; before vegetation removed
3. Lids; after vegetation removed

Key

H1

Mean
± SE
n

Pools, Lawns, Hummocks

- Required level
- No. cores in group
- Mean level achieved ±SE. Arrow indicates direction of change from previous stage; no arrow indicates no change.
- No. records
- Core numbers of group

and aluminium foil to 'seal' in the sampler. For the second phase gas samples were collected from all cores, and bucket lids were used as covers since they were found to give a satisfactory seal against gas leakage when fully clipped on. This method was adopted for all subsequent stages. Throughout the Pre I stage the required water levels were 0 cm, -3 cm and -10 cm for pools, lawns and hummocks, respectively. These were chosen to represent the mean field water level of each microhabitat at the time of collection. The surface vegetation on all cores was left intact.

For each microhabitat four cores acted as 'controls', and the required water level in these remained unaltered from the initial Pre I stage level throughout the garden experiment.

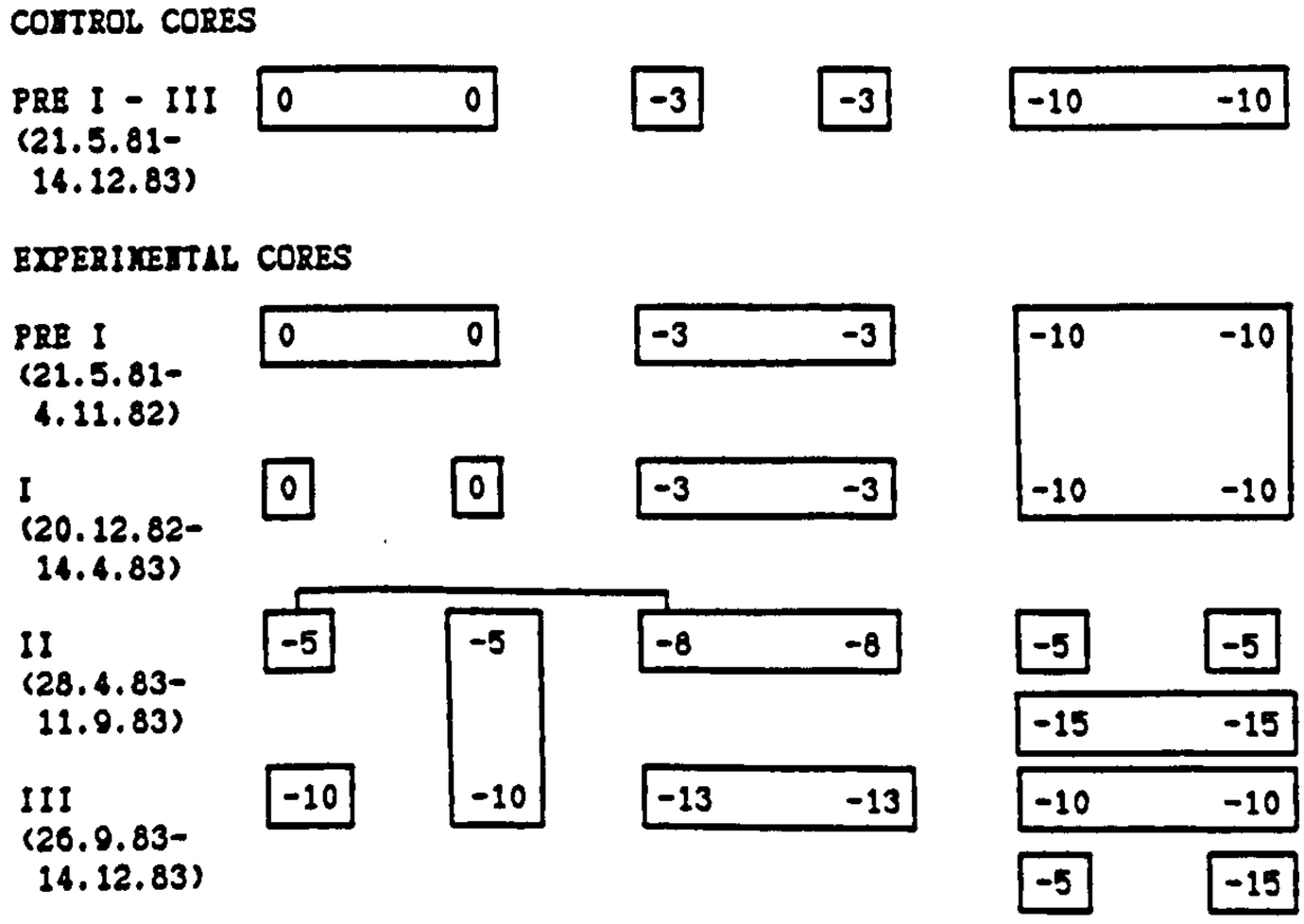
After the Pre I stage, half the cores (experimental and controls) had their surface (green) vegetation removed. The water levels in each core were unaltered for stage I, in order to record the effect of removing the green matter on surface gas fluxes. Stage I was completed in April 1983, after 16 weeks, and the water levels altered ready for stage II, as indicated in Table 4.3. Stage III began in September after further water level alterations.

Table 4.3 also gives details of the water levels achieved, for comparison with those required. There was more variation in the measured water levels than had been hoped for, and analyses were carried out to determine which differences were significant. Parametric or non-parametric tests were used, depending on the results of an initial analysis of variance to detect significant differences between the water levels of individual cores within the same control or experimental group, and on the number of data in each set. Subsequent tests, between control or experimental groups, were either paired (paired t-test or Wilcoxon signed-rank test) or unpaired (t-test or Mann-Whitney U test) depending on whether the comparison being tested was within or between the different experimental stages. In relation to Fig. 4.13, in which the results are presented, this equates with comparisons between the relevant values in any given row or column, but not diagonally. In the Figure, the comparisons which yielded a non-significant result are grouped together in a box, or

linked by a line. The value in each box is the required water level. In these analyses, all stages of control groups were treated together.

From Fig. 4.13 it can be seen that, in practice, there was more variation in water levels than had been planned. The regulation of the pool water levels proved most difficult, since the pool peat surface followed the water level; if water was added, the peat expanded and if water was siphoned off, the peat surface fell with it. Hence it was not possible to maintain any significant depth of free water above the pool peat as in the field situation. It was possible to lower the water level beyond the level to which peat shrinkage kept pace, but the peat above the water level remained fully saturated. This was not the case for either lawn or hummock peat, which remained moist, but not saturated, above the imposed water level.

FIG. 4.13 Summary diagram of results from garden water level analyses. cm, relative to peat surface. For further explanation, see text.



Water levels were initially measured relative to the rim of their bucket and the level relative to the peat calculated from this and the most recent measurement of the peat surface relative to the bucket rim. The mean values given in Table 4.3 thus assume no growth of the peat between water level measurements. The height of the peat surface was measured in each bucket on three occasions during the study

period, as indicated in Fig. 4.1a. The upward growth of the peat surface of the garden cores was, however, significant (see Appendix I) and thus the real water level relative to the peat surface of each core was probably dropping gradually over the period between peat measurements, leading to possible underestimates of the mean values in Table 4.3. After each measurement of the peat surface the water levels were altered as necessary to bring them to those required. This was done between stages of the garden experiment. (It should be emphasised that the apparent 'growth' of the pool peat indicated in Appendix I is mostly, if not all, attributable to the buoyancy of the suspended peat material when the water level in the core was increased.)

The potential error introduced by the indirect method of water level measurement in the cores was assessed by estimating the real water level in each core relative to the peat surface for each water level measurement, assuming a constant rate of upward growth of the surface. These derived values were subjected to the same statistical analyses as were the original measurements. The results were much more negative (deeper) than the originals, and more control and experimental core groups yielded a significantly different result. Mean values such as -29.9 cm (CH, stage III) and -39.2 cm (CL, stage III), in a bucket which is, with fitted extension, approximately 50 cm deep, are clearly overestimates, and had any such measurements been made in the garden the error would have been noticed immediately and the offending water levels changed. No such obvious errors were noted, however, and it is concluded that such derived estimates introduce more frequent and larger errors than are likely to be present in the original data. This being so, the results shown in Appendix I will be used for the water level régime summary against which to interpret the garden gas flux results, while keeping in mind that some of the values may be slightly underestimated.

The water level in M1 was not regulated and its surface vegetation was not removed throughout the garden experiment. The overall mean water level in M1 for the entire study period was -6.2 cm, but the wide variation due to natural fluctuations was reflected in the large standard error (±1.3 cm, Table 4.3). There was

considerable variation between years; in 1981 the minibog retained a relatively high water level (around -5 cm), even through the summer months, whereas in 1982 it fell below -10 cm on several occasions. The level dropped from about -5 cm in early summer 1983 to around -40 cm in August, and remained very low at least until December, when the last record was made (-25 cm).

FIELD

a) Introduction

In the field, measurements of the water levels relative to the bottomless bucket rims were measured on every field visit and were used in the calculation of the surface gas flux. Water levels relative to the peat surface were recorded from August 1982 at CR and from September 1982 at MH. Prior to this, it had been assumed that the rims had remained at a constant height above the peat surface, but this was discovered not to be the case (because of the pressure put on them when sealing the lids on for sampling), and so it was not possible to relate the measurements to the peat surface. These data have been omitted from the present analyses. The rest of the data

TABLE 4.4 Summary of ANOVA results; Moor House water levels. All data.

Treatment	Significance level
TIME	***
HABITAT	***
CUT	***
TIME.HABITAT	***
TIME.CUT	NS
HAB.CUT	NS
TIME.HAB.CUT	NS
SITE	***
TIME.SITE	NS
HAB.SITE	**
CUT.SITE	NS

have been analysed for seasonal trends, and to assess the extent and significance of any differences between the two field Sites, between different sampling areas (sites) at the two Sites, and between the

microhabitats represented, which might be reflected in the concurrent gas flux record.

b) The effect of the buckets on internal water levels

The installation of vertically-positioned cylinders in the peat to delimit a sampling area affected the natural level of water inside (see Appendix J), presumably by restricting lateral flow. The extent to which the internal water level was affected differed between sampling sites both at MH and CR. In addition, there was variation between buckets at each site, though at MH any small microhabitat effect was not consistent between sites. At MH, sites 4-6 were most extreme, compared to smaller effects seen at the other sampling sites. At CR the deviations were, in general, larger, though site 17 was a noteable exception. These results point to a complex relationship between the internal and external water levels, probably reflecting an integrated response to factors such as physical structure and degree of humification (which affect hydraulic conductance) in and around the bucket, the general (seasonal) water level and the specific level in the immediate vicinity of the bucket resulting from recent weather conditions, the position of the bottom of the bucket in relation to the peat profile, and the surface vegetation. Only when there are extreme weather conditions do these appear to dominate and cause noticeable, consistent effects over the bog as a whole. It is clear that to unravel the cause and effect of all the internal water level deviations was beyond the scope of the present study. In most cases the deviations were less than 2.5 cm, and even in those cases where they were larger the accuracy of the calculation of the surface gas flux is not affected. However, the modification to the natural fluctuations in water level, and potentially, therefore, to the surface flux and to the extent of the sulphide zone should be borne in mind when interpreting the results.

The analyses of water levels reported below for MH and CR refer to the internal water levels.

c) Moor House

Table 4.4 summarises the results of the analyses of variance carried out on the MH water level data to assess the significance of

four factors: time, microhabitat, removal of the surface green matter and sampling site. Some interactions between these factors were also tested. In Table 4.5 are presented some of the descriptive statistics relating to the analyses.

Each of the four main factors were significantly correlated with the water level ($p<0.001$). The seasonal changes for each microhabitat, both uncut and cut, are shown in Fig. 4.14, in which the means of three values are plotted. As indicated by the significant ($p<0.001$) TIME.HABITAT interaction, the seasonal fluctuations are not the same for each microhabitat. The discrepancy in the small-scale

TABLE 4.5 Selected Moor House water level statistics.

Treatment	Factor	Mean (cm)	SE (cm)	n
Habitat	Pool	+8.3	0.9	48
	Lawn	-1.4	0.5	48
	Hummock	-14.7	0.9	48
Cut	Uncut	-4.1	1.4	72
	Cut	-1.0	1.2	72
Site	4-6	-4.6	1.7	48
	7-9	-0.7	1.6	48
	10-12	-2.4	1.5	49

Grand mean = -2.6 ±0.9 cm

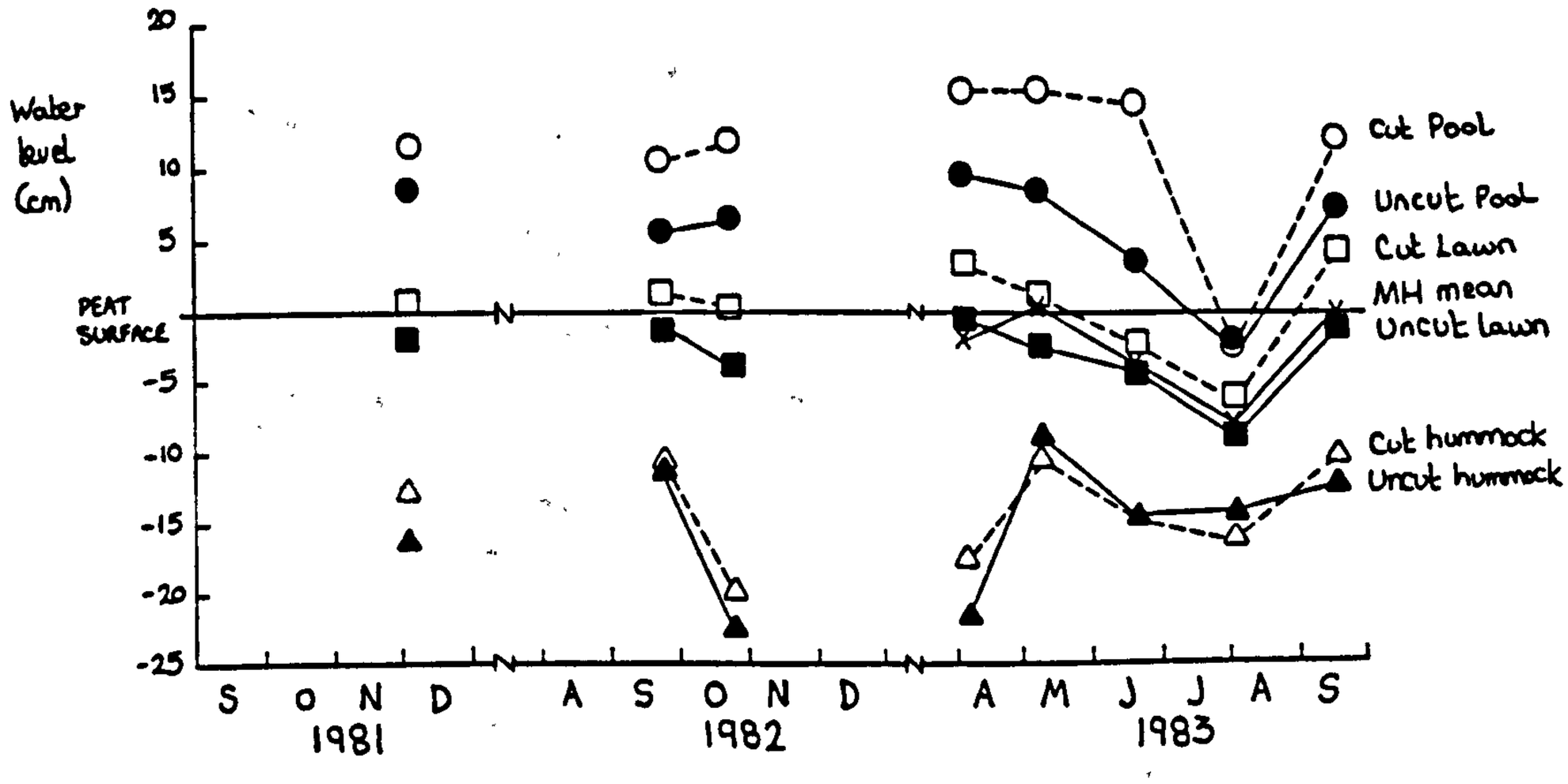
fluctuations between the microhabitats is probably related to the position in the peat profile of the water level, the degree of humification there and hence the resistance, or otherwise, to any lateral flow. In all cases the water level during the first visit of 1983 was slightly higher than it had been at the end of the 1982 field season (October for MH). From the limited data available here, the water levels appeared to recover more rapidly than they fell.

In nearly every case the effect of removing the surface green matter was apparently to increase the water level, on average, by 3 cm ($p<0.001$). This is an artefact resulting from the change in the height of the moss surface. In terms of its position relative to the peat profile, there is no reason to suspect that the water levels

differed significantly between uncut and cut areas for any given microhabitat at a sampling site. The hummocks did not show such a clear distinction between uncut and cut area water levels; this may in part have been due to the difficulty of making such accurate measurements deeper down in the peat.

As expected, the water levels of the three microhabitats were significantly different ($p<0.001$), the mean levels (±SE) being 8.3 ±0.9 cm (pools), -1.4 ±0.5 cm (lawns), and -14.7 ±0.9 cm (hummocks), over the period of the study. The differences were distinct on each visit, as seen in Fig. 4.14. In general, the lawn water levels were more similar in their height and behaviour to those of the pools than they were to the hummocks. Despite different mean absolute water levels, the range shown by each microhabitat was very similar, about 25 cm, for the period recorded.

FIG. 4.14 Seasonal changes in Moor House water levels, 1981-1983. Means of 3.



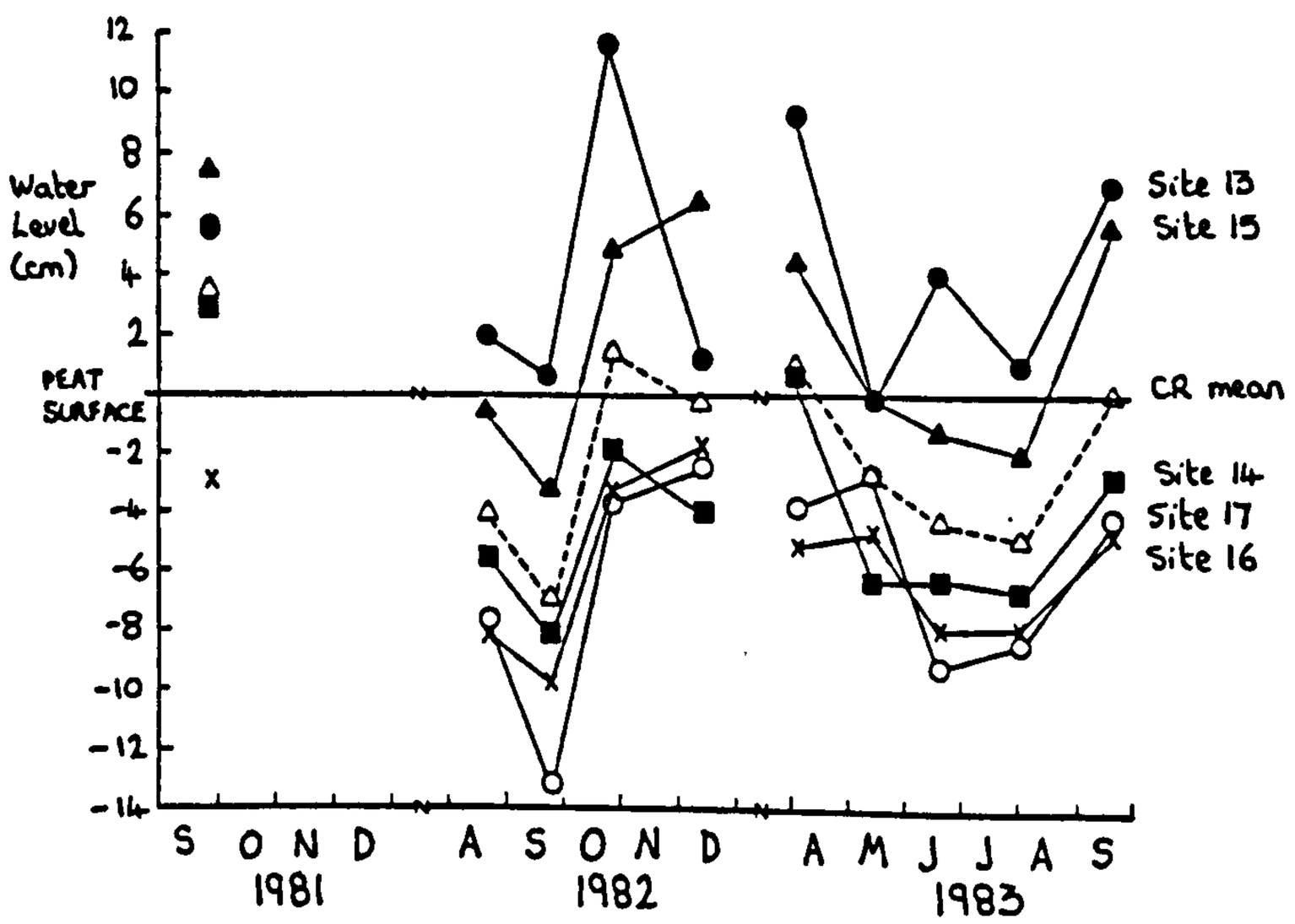
The data from each group of sampling sites were also compared, and shown to be highly significant ($p<0.001$), indicating that the three areas chosen were not strictly replicates in terms of their water level régimes. The overall wettest sampling site area was site 7-9, mean water level -0.7 cm, and the driest area site 4-6, mean water level -4.6 cm. At site 10-12 the mean water level was -2.4 cm.

The seasonal effect was consistent between all three areas, as was that of removing the green surface vegetation, but the HABITAT.SITE interaction ANOVA returned a significant ($p<0.01$) result, indicating that at each site the three microhabitats contribute differentially to the variation. Over the three sites, the mean range (mean maximum - mean minimum) of the hummock water levels was 6.7 cm, that of the pools 6.0 cm and that of the lawns 1.4 cm; thus the hummock and pool water levels were most variable (Fig. 4.14). Water levels at sites 4-6 and 10-12 were more variable than at site 7-9.

d) Coom Rigg

The overall mean water level at CR was -1.7 ±0.6 cm, compared with -2.6 ±0.9 cm at MH. The lowest (deepest) and highest levels recorded at CR were -19.0 cm and 16.0 cm (cf -29.0 cm and 17.0 cm at MH).

FIG. 4.15 Seasonal changes in Coom Rigg water levels, 1981-1983



The seasonal fluctuations in water level recorded at CR are shown in Fig. 4.15. The sampling site mean (n=4) is plotted for each visit, and the overall CR mean water level is added. As was seen for the MH data, at CR there was a general increase in the height of the water level in the autumn and a fall-off during the spring and early summer.

TABLE 4.6 Summary of ANOVA results, Coom Rigg water levels. All data.

Treatment	Significance level
TIME	***
SITE	***
CUT	***
TIME.SITE	***
TIME.CUT	***
SITE.CUT	***

The seasonal effect was significant ($p<0.001$; Table 4.6). In 1982 the lowest water level recorded at each site was in September. In the 1983 season minimum site records were not simultaneous, occurring on different site visits made between May and August. The overall mean water level showed an increase of only 1.3 cm between the final 1982 visit in December and the first records of 1983 in early April, but individual site means varied considerably in this respect, from an increase of 8.0 cm at site 13, to a decrease of 3.3 cm at site 16. This is likely to be related to the physical nature of the peat below each site and the position of the site on the bog, since these observations are in line with the overall site mean water levels (Table 4.7) which indicate site 13 to be the wettest site (mean 4.0 ±0.8 cm) and site 16 the driest (mean -5.5 ±1.2 cm). Individual site mean water levels (Table 4.7) increased in wetness in the order 16 (-5.5 cm), 17 (-5.1 cm), 14 (-4.0 cm), 15 (2.0 cm), 13 (4.0 cm). This

TABLE 4.7 Selected Coom Rigg water level statistics.

Treatment	Factor	Mean (cm)	SE (cm)	n
Site	13	+4.0	0.8	40
	14	-4.0	1.4	40
	15	+2.0	0.9	40
	16	-5.5	1.2	38
	17	-5.1	1.0	40
Cut	Uncut	-4.1	0.7	99
	Cut	+0.6	0.8	99

Grand mean = -1.7 ±0.6 cm

sequence does not run parallel to the serial location of the sites across the bog.

Although there is no highly developed pool-hummock complex at CR there is a small-scale surface patchiness of contrasting 'wet lawn' areas and drier 'low hummocks'. On installing the sampling cylinders, the exact position of each was chosen to represent an even proportion of both types, and so two buckets out of the four at each site were designated 'wet' and two 'dry'. These designations were subjective at each site and were not comparable between sites. Although there is no habitat factor, as for MH, the analysis of individual bucket mean water levels for each site indicated that there was a significant difference between buckets at sites 14, 16 ($p<0.001$) and 17 ($p<0.01$), but no such difference at sites 13 and 15 (Table 4.8). This may be explained by the fact that at the wetter sites (13 and 15), where the

TABLE 4.8 Summary of water level ANOVA results and selected statistics for individual buckets and effect of cutting at each Coom Rigg site.

Bucket label	Uncut/ Cut	Mean water level (cm)	Individual buckets sig. level	Mean water level (cm)	Cut vs uncut sig. level
13/57	U	-4.9			
13/59	U	+2.0	NS	+3.4 (U)	NS
13/58	C	+4.1		+4.6 (C)	
13/82	C	+5.1			
14/61	U	-9.4			
14/63	U	-0.2	***	-4.8 (U)	NS
14/60	C	-12.9		-3.2 (C)	
14/62	C	-6.5			
15/53	U	+1.0			
15/55	U	-3.2	NS	-1.1 (U)	***
15/54	C	+5.4		+5.1 (C)	
15/56	C	+4.9			
16/48	U	-4.0			
16/69	U	-14.8	***	-9.1 (U)	**
16/47	C	+2.4		-2.0 (C)	
16/68	C	-6.8			
17/50	U	-9.2			
17/52	U	-8.4	**	-8.8 (U)	***
17/49	C	-1.4		-1.4 (C)	
17/51	C	-1.4			

mean site water levels indicate standing water (i.e. a +ve value) the general level is dependent on precipitation and surface flow, since the entire peat profile is waterlogged, and hence large differences in water level behaviour would not be expected between buckets. In contrast, at the drier sites, where the mean site water levels were all below the peat surface, the fluctuations in water level will be dependent on the physical nature of the peat, in addition to the precipitation, and it is known that peat structure may vary considerably over very small distances (see Section 2.4).

As at MH, removal of the green matter resulted in an apparent 'increase' in the water level of 4.7 cm (Table 4.7, cf 3.1 cm at MH), and is probably an artefact.

4.2 SURFACE GAS FLUX

4.2.1 INTRODUCTION

In the following account of surface gas flux results, methane and carbon dioxide are dealt with in turn and, within this, the garden results are described first followed by those from the field sites. For each set of results (garden and field) the main effects of temperature, water level (individually and then their relative effects) and of removing the green matter are described (for the three microhabitats separately where relevant). To help in following the detailed accounts of the results given below, a summary of the factors investigated which were most closely associated with surface gas flux is presented in Tables 4.11 and 4.12, below, for the garden and field peat, respectively.

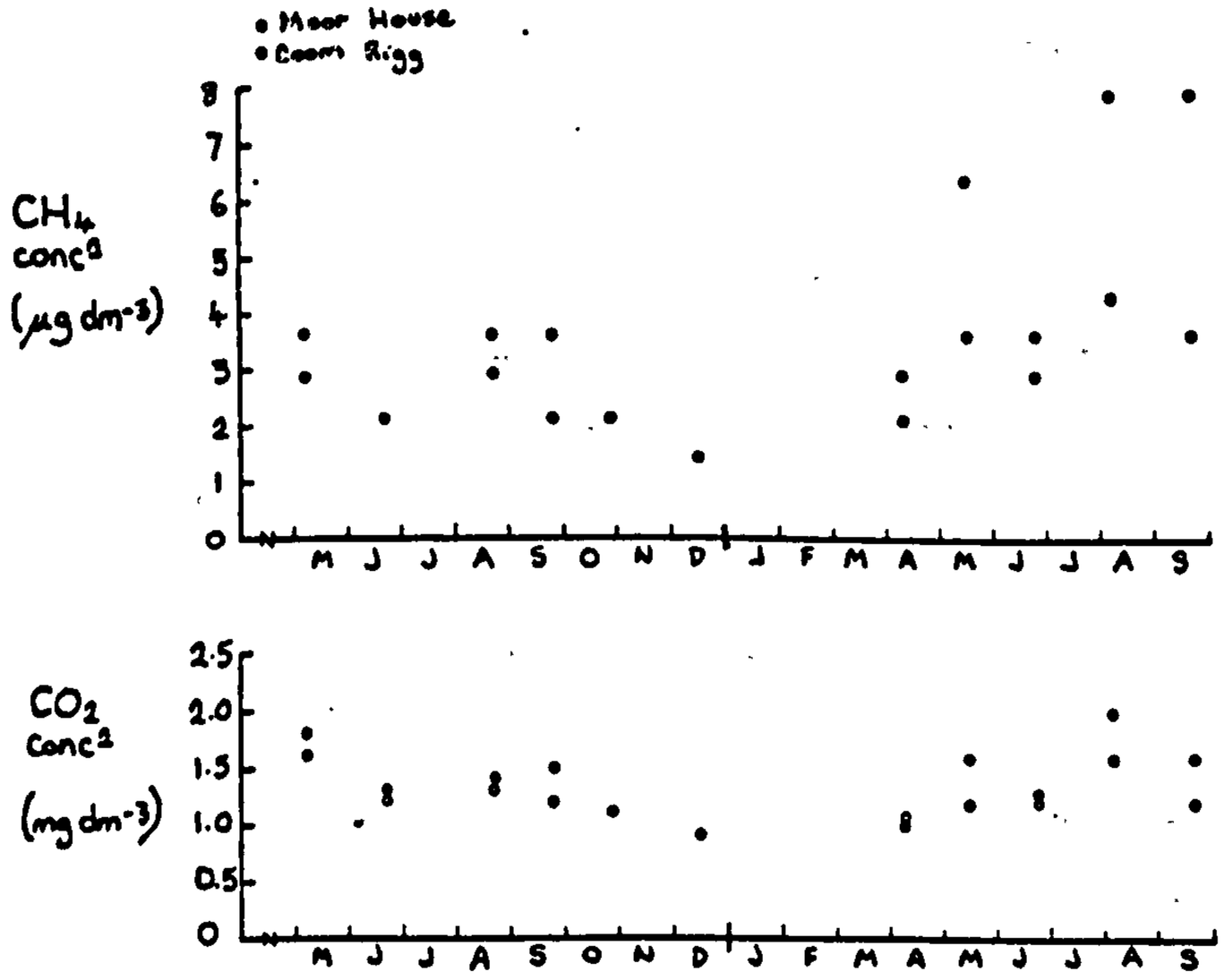
Flux ($ML^{-2}T^{-1}$) is reported as the mass of carbon lost as methane (CH_4-C) or carbon dioxide (CO_2-C). The method used to calculate the flux from the concentration is given in Appendix H). Throughout, a positive flux value represents a net increase in the component concentration in the sampler over the sampling period, i.e. strictly an efflux from the peat. A negative value therefore represents an influx to the peat: the peat is a sink not a source. In reporting the garden flux results, an arrow (→) has been used to denote the contrast

between conditions in two different stages of the garden experiment, represented as Pre I, I, II and III. Thus, 'I→II' means the difference between stages I and II, in water level, gas flux, temperature or whatever factor is under discussion. All abbreviations, symbols and conventions used are explained in 'Abbreviations and Conventions' at the beginning of the thesis.

The garden surface gas flux data analysed here were collected between May 1981 and December 1983 (see Fig. 4.1a, above). The field results refer to data from the surface gas samples collected between May 1982 and September 1983.

Because only a limited number of samples could be analysed, initial samples of the atmosphere enclosed in the bucket around the samplers were not taken in the field, in contrast to the garden sampling régime. Instead, a sample of the ambient atmosphere at 1.5 m above the bog surface was taken at each Site when the gas samples were collected (Fig. 4.16), and the concentration of components in this sample was taken as the initial concentration of gases around the

FIG. 4.16 Ambient gas concentration at Moor House and Coom Rigg, 1982-1983. Samples taken at +150 cm.



samplers, from which the change in concentration over the sampling period were calculated. Unfortunately, no 'initial enclosed air' samples were ever collected in the field and in order to assess, roughly, the extent of any errors which might occur in the calculation a paired t-test was carried out between concentrations of each component in initial enclosed and ambient air samples collected routinely in the garden. Each microhabitat was treated separately in the analysis, as were 'uncut' and 'cut' sampling areas; there were 22 pairs of data for each. There was no difference in the carbon dioxide concentration of initial enclosed and ambient gas samples for any of the six different sampling area types, and no difference in the CH_4-C concentration of the paired samples above hummocks, but whereas uncut lawns showed no difference, cut lawn and uncut pool data returned a 5% significance level for the differences, and cut pools gave $p<0.001$. In all cases the concentration was higher in the enclosed than in the ambient air samples, and in both lawns and pools the most significant differences were seen over cut sampling areas. The mean absolute difference between the concentration in the paired samples from uncut pool cores was 0.25 mg dm^{-3} (≡0.25 ppm) methane, and, assuming the (cylindrical) gas collecting space to be 20 cm high (that is, the rim of the bottomless bucket to be 20 cm above the water level) and the sample period to be 48h, this would give rise to an overestimate of CH_4-C of 19 mg m^{-2} d^{-1} (about 59% of a median result). This is the worst case; for cut pool microhabitats and cut lawns, the corresponding overestimates, on average, are 7.5 mg m^{-2} d^{-1} (or about 42% of a 'typical' result) and 1.5 mg m^{-2} d^{-1} (3%) CH_4-C. These error estimates are based on garden data, where ambient methane concentrations were lower, and carbon dioxide higher, than those from the field. They do not, therefore, represent accurate error margins arising from the field sampling methods, but suggest that such errors may have been involved, and, if so, would lead to an underestimate of the initial enclosed sample methane concentration and hence to an overestimate of the surface flux over lawns and, to a greater extent, pools. In the field, however, wind speed is much greater than in the garden, particularly at MH, and this will increase the possibility of any methane being dispersed as soon as it is evolved, and thus reduce

any difference between its concentration inside and outside the collecting bucket prior to sealing the lid for sampling.

4.2.2 CORRESPONDENCE BETWEEN REPLICATE SAMPLES

As has been described previously (Section 3.3.3, Arrangement of Peat Gas Samplers), the replication of samples at MH was between sites. At CR, where no clear-cut microhabitats were available, replication was within each site. Duplicate buckets for both uncut and cut areas were present at each site, adjacent to one another.

TABLE 4.9 Selected Moor House surface gas flux statistics.

Treatment	Factor	CH_4-C (mg m^{-2} d^{-1})			CO_2-C (mg m^{-2} d^{-1})		
		n	Mean	SE	n	Mean	SE
Site	4-6	60	11.3	±1.4	60	191	±30
	7-9	60	7.0	±1.3	60	178	±29
	10-12	60	19.4	±3.7	60	125	±20
Habitat	Pool	60	16.0	±2.6	59	71	±11
	Lawn	60	17.3	±3.1	60	71	±12
	Hummock	60	4.4	±0.8	60	352	±31
Cut	Uncut	90	16.8	±2.3	89	176	±19
	Cut	90	8.4	±1.6	90	153	±24
All data		180	12.6	±1.4	179	165	±15

Analyses of variance, carried out to determine whether replicate gas samples were statistically so, returned highly significant results at MH for the SITE treatment ($p<0.001$ for both CH_4 and CO_2 effluxes; Table 4.15). The mean flux for each MH site is shown in Table 4.9. The SITE effect of the MH water level analysis of variance was also highly significant (Table 4.4).

The results from similar 'between bucket' ANOVAs for CR are shown in Table 4.10. There was no significant difference in the flux of the components from the different buckets at site 17. Overall, the differences in CH_4-C flux were most significant, but at site 14 CO_2-C also returned a highly significant result ($p<0.001$). The corresponding CR water level analyses of variance gave a non-

significant result for the differences in the water levels of the buckets at sites 13 and 15, but were highly significant ($p<0.01$) for the remaining three sites.

TABLE 4.10 Summary of results from ANOVAs to test for surface gas sample replication at Coom Rigg.

Site	CH_4	CO_2
13	**	NS
14	***	***
15	*	*
16	***	*
17	NS	NS

4.2.3 SUMMARY OF MAIN FACTORS ASSOCIATED WITH SURFACE GAS FLUX

Tables 4.11 and 4.12 summarise the associations between temperature and water level and gas flux as suggested by the detailed garden and field results in the following sections.

TABLE 4.11 A summary of the associations between temperature and water level, and gas flux, as suggested by the garden results. For further details see text.

a) association between gas flux and temperature

	Pool	Lawn	Hummock
CH_4	+	+	+
CO_2	+	+	+
O_2	(+)?	(+)?	(+)?

b) association between gas flux and water level

	Pool	Lawn	Hummock
CH_4	(-)?	-	(+)?
CO_2	+(-)	+	-
O_2	(+)?	(-)?	?

\+ correlation likely
\- no clear indication of a correlation
? results unclear
( ) possible interpretation, though some confounding results

TABLE 4.12 A summary of temperature and water level effects on gas flux, as suggested by the field results.

a) Temperature effect

DATA Site	Micro-habitat	Cut / Uncut	Comparison	CH_4	CO_2	O_2
MH	Pool	Uncut	Within pools	+	+	?(+)
MH	Lawn	Uncut	Within lawns	+	+	?(+)
MH	Hummock	Uncut	Within hummocks	+ small	+	?(+)
CR	-	Uncut	Within uncut areas	+	+	?

b) Water level effect

DATA Site	Micro-habitat	Cut / Uncut	Comparison	CH_4	CO_2	O_2
MH	Pool	Uncut	Within pools	-	+	(+)
MH	Lawn	Uncut	Within lawns	(-)	+	(+)
MH	Hummock	Uncut	Within hummocks	(-)	-	(+)
MH	Pool	Cut	Between microhabitats	+	+	+
MH	Lawn	Cut				
MH	Hummock	Cut				
MH	Pool	C&U	Between microhabitats	+	+	+
MH	Lawn	C&U				
MH	Hummock	C&U				
CR	Wet	Cut	Between habitat types	?(small)	+	+
CR	Dry	Cut				

Parentheses indicate a tentative conclusion

4.2.4 METHANE EFFLUX

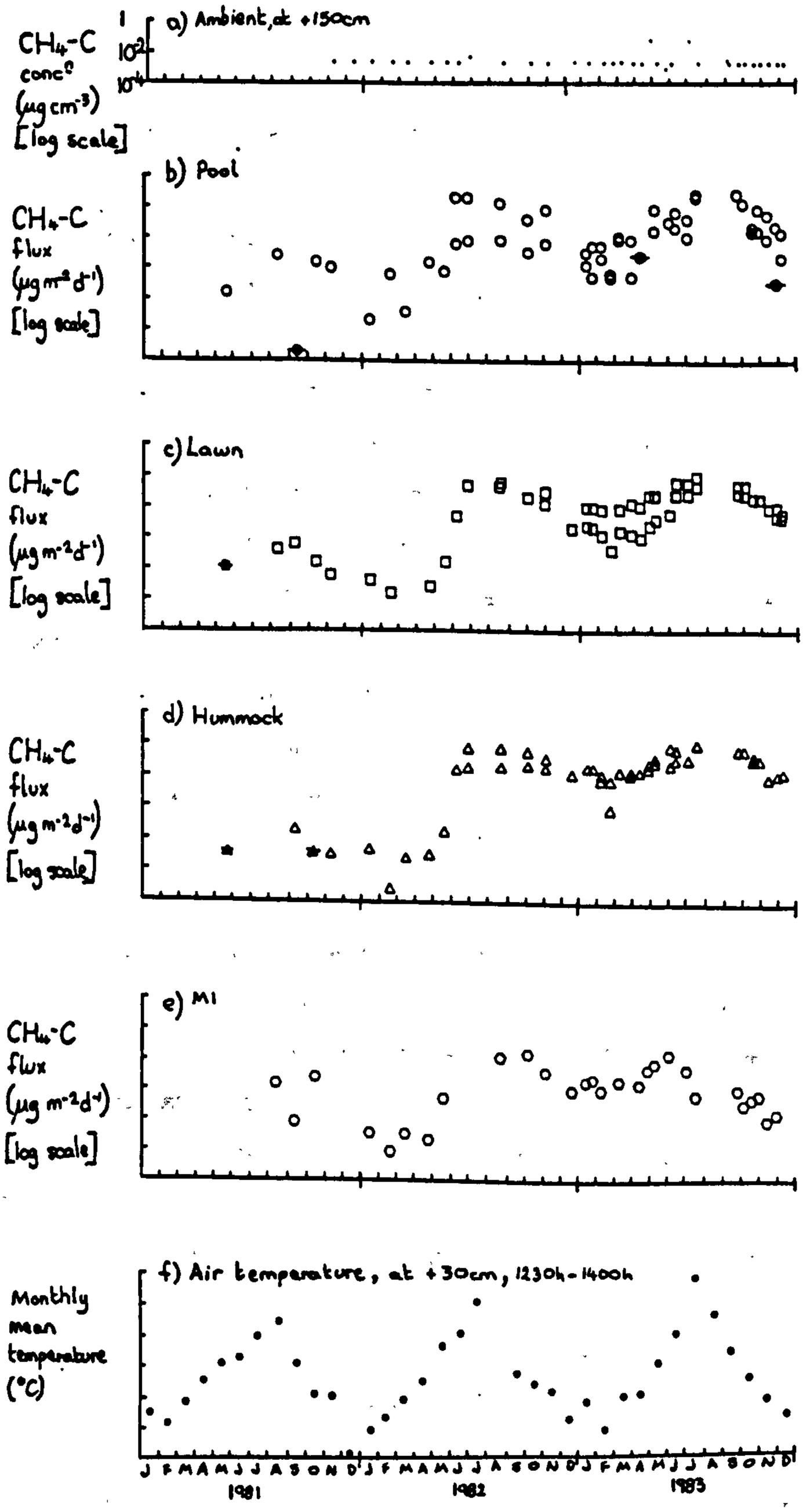
SEASONAL CHANGES

a) Garden

Of the 35 samples of garden air taken between November 1981 and December 1983, 29 showed a CH_4-C concentration of 1.4×10^{-3} ppm (2 vpm). The lowest concentration recorded was 7.1×10^{-4} ppm (May and July 1983), and the highest 2.1×10^{-2} ppm (April 1983). Thus, there was no apparent seasonal trend in ambient methane concentration.

Seasonal changes in surface garden CH_4-C flux are given in Fig. 4.17b-e, in which individual results are plotted from the two uncut

FIG. 4.17 Seasonal changes in garden surface methane flux. Individual uncut control core data.



Open symbols represent an efflux, closed symbols an influx.

control cores from each microhabitat, and from M1. The water level in the control cores was kept constant throughout, but that in M1 was allowed to fluctuate naturally. Air temperatures are shown in Fig. 4.17f.

Each plot shows very clearly the effect of using the bucket lids to seal the buckets (from June 1982 onwards) rather than aluminium foil and black polythene. Up to that time the absolute flux values are lower; after the lids were fitted the scatter was much reduced and leakage of gas from the buckets during sampling appears to have been stemmed.

CH_4-C flux shows a similar, marked seasonal trend for all microhabitats, including the minibog M1, although the M1 results are slightly more erratic than those of the controls. This is presumably attributable to the compound effects of temperature and water level changes and also to the inability to effect a seal around the rim of the upturned bucket when the water level was very low, because of damage and disturbance. Considering the results from June 1982 onwards, the CH_4-C flux picked up from about 1 mg m^{-2} d^{-1} in February, its annual minimum for all microhabitats, and peaked between July and September, at about 100 mg m^{-2} d^{-1}. The absolute maximum value was more dependent on the microhabitat than was the minimum, there being a range of 50 to 250 mg m^{-2} d^{-1} between highest and lowest maximum values, compared with only 0.4 to 1.0 mg m^{-2} d^{-1} between the minimum values. The maximum CH_4-C fluxes recorded for pool, lawn and hummock in 1983 were larger than their respective maxima in 1982, apparently reflecting the higher summer temperatures that year. It is interesting to note that there was a time lag between the maximum peat and air temperature (July) and the maximum CH_4 flux in 1983 (September).

A comparison of the median flux for each microhabitat reveals that between December and April hummock methane flux is greater than that of the pools. Between May and November the situation is reversed and pools evolve more methane than do hummocks. Hence the highest mean flux measured each year is over pools. The lawn median methane flux was almost invariably lower than that of both pools and hummocks at all times of the year. Further, the annual mean fluxes of methane

(1983 data) from pools, lawns and hummocks, are in the same rank order: 45, 18 and 37 mg m^{-2} d^{-1} CH_4-C, respectively, omitting any negative fluxes from the calculation. The corresponding annual mean CH_4-C flux from the minibog was 2.5 mg m^{-2} d^{-1}. Much of this comparatively low flux is attributable to the persistent low methane fluxes from July to December, 1983.

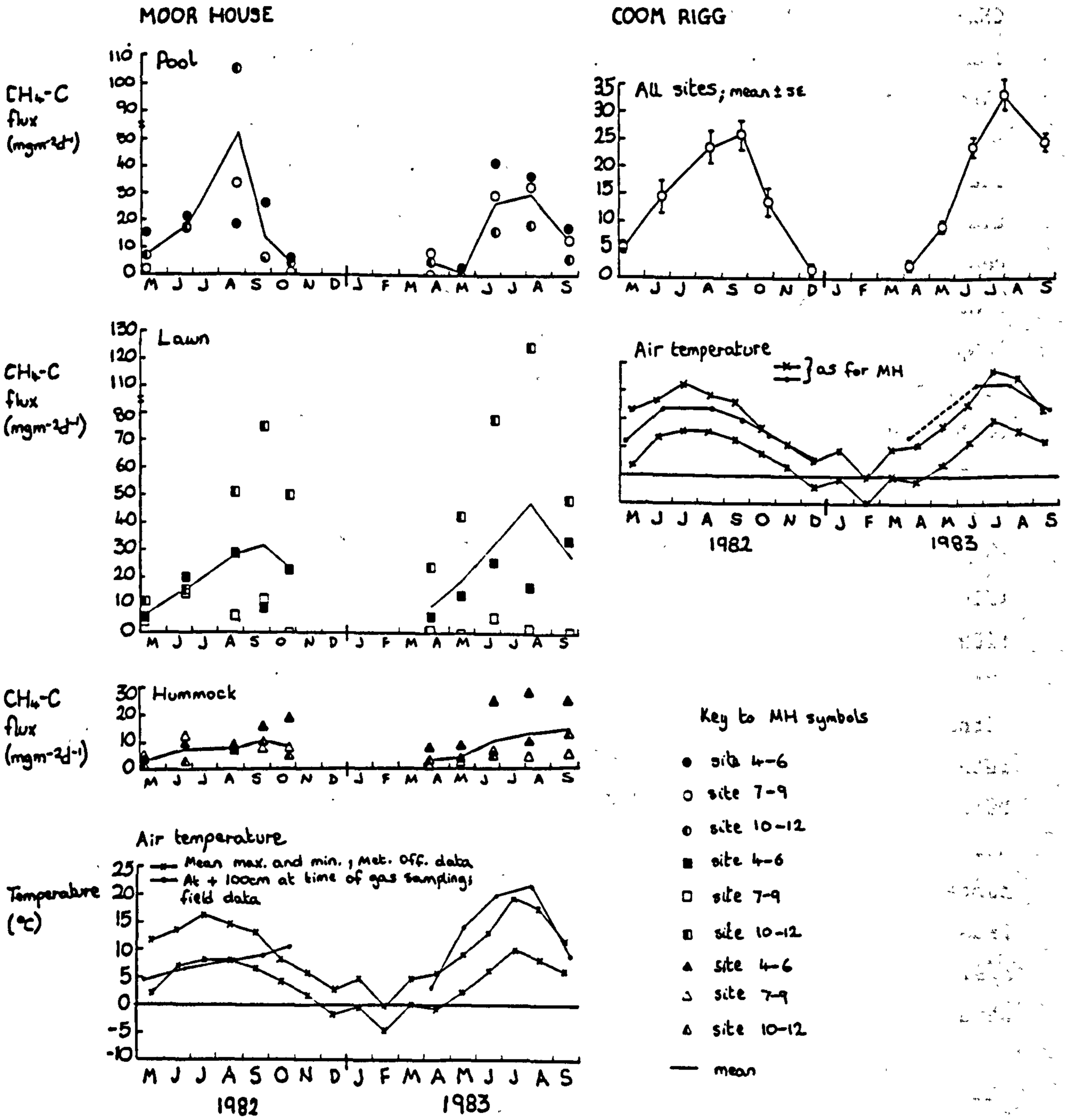
It is clear that methane flux is temperature-dependent, though the difference between the absolute fluxes from the three microhabitats (and possibly the smaller annual range of the M1 results) suggest it is not exclusively so. The gross patterns of seasonal change corresponded closely with those of air (and peat) temperatures, but a more detailed comparison between Fig. 4.17 and weather records revealed that small-scale, short-term temperature changes were not reflected in flux measurements. Minimum methane flux corresponds with the period of maximum snow-lie (Fig. G.3, p.449), but the snow was cleared before the samplers were put out, and since the same period experienced the highest frequency of ice and frost days (Fig. G.2, p.449) it seems more likely that the decline in methane flux was again a temperature effect.

One or two records per year (April to December) showed a negative methane flux, i.e. a net sink of methane into the peat. A negative methane flux has been recorded between July and January in the Great Dismal Swamp, Virginia, by Harriss & Sebacher (1982). In the present study it occurred most often in pools and least often in lawns. The number of such records per year declined from five to two after bucket lids were used during sampling, and was thereafter seen only in pools, again between April and December. There is no obvious correspondence with erratic weather patterns.

b) Field

Fig. 4.16 (Section 4.2.1, Surface Gas Flux) gave the ambient CH_4-C *concentrations* at MH and CR (at +1.5 m) on each field visit. The seasonal change in CH_4-C *flux* at the surface of the bogs is shown in Fig. 4.18. The mean fluxes over the uncut sampling areas for each field visit are given, and because the SITE effect was significant at MH, the individual site fluxes are also shown. For CR the

FIG. 4.18 Seasonal changes in surface methane flux at Moor House and Coom Rigg, 1982-1983. Uncut sampling area data.



(significant) SITE effect is shown by standard error bars, to simplify the graphs.

The seasonal changes in CH_4-C flux were highly significant ($p<0.001$) at MH, but were less marked over hummocks than over pools and lawns. There was a maximum difference of only 7 mg m^{-2} d^{-1} between the mean CH_4-C fluxes of all the microhabitats on the first field visit of the year (1982 and 1983 data), but maximum mean fluxes varied more widely, both between years and between microhabitats. Over pools, the 1982 mean CH_4-C flux increased over five-fold to its August peak of 52 mg m^{-2} d^{-1}, compared to slightly less than a six-fold increase in 1983 to its peak, again in August, of 29 mg m^{-2} d^{-1}. The overall rate of increase in the two years was similar, taking into account the extra April record in 1983, but the absolute minimum and maximum fluxes in 1983 were respectively 37% and 44% lower than those in 1982, despite the higher mean air temperature. In both years the decrease in flux over the month following its peak was rapid. The seasonal trends in flux followed closely those of the air temperature, although in both years the peak flux occurred in the month following the peak (maximum and minimum) air temperature.

The variation in flux between sites was greater at warmer times of the year than during cooler periods, and this trend was more marked in 1982 than in 1983. In 1982 the minimum range of individual site fluxes was 5 mg m^{-2} d^{-1}, recorded in October, and the maximum was 87 mg m^{-2} d^{-1}, in August. In 1983 the minimum range was 3 mg m^{-2} d^{-1}, in May, and the maximum was 25 mg m^{-2} d^{-1}, in July.

In both years the CH_4-C flux over lawns increased from the first record of the season to its summer peak but the 1982 peak was lower than that in 1983, in contrast to the situation over pools. The minimum mean flux, recorded on the first visit of each year over lawns, was between 5 and 10 mg m^{-2} d^{-1}. In 1982 this increased four and a half times, to 32 mg m^{-2} d^{-1} in September, and in 1983 the increase was also four and a half times, to 48 mg m^{-2} d^{-1}, in August. Hence, the difference in 1982 and 1983 mean minimum recorded fluxes was 3 mg m^{-2} d^{-1}; and, as over the pools, the difference between the maxima of 1982 and 1983 was considerably larger (16 mg m^{-2} d^{-1}). The variation between methane flux at different sites was rather higher

than was seen over pools, but again there was evidence for a summer increase in the range.

The lawn methane flux corresponded well with the (Met. Off.) temperature, perhaps more so than that of the pools in that the lower 1982 temperatures were apparently reflected in lower summer methane fluxes above lawns. Peak flux in 1982 occurred about two months behind that of the air temperature, and in 1983 about a month later.

The amount of carbon lost as methane from hummocks was much reduced compared to that from lawns or pools. Of the ten field visits, only two showed methane flux to be greater than 10 mg m^{-2} d^{-1}. There was a slow increase in flux in both years, peaking in September, at 10 and 14 mg m^{-2} d^{-1} for 1982 and 1983, respectively. The minimum flux in both years was 2-3 mg m^{-2} d^{-1}. The range of the individual site records was smallest at the beginning of the season (around 4 mg m^{-2} d^{-1}) and increased thereafter. This general pattern, with relatively high variation at the end of the season, was also seen above lawns, but the site variation above pools had decreased noticeably by this time. Temperature appears to have a much less direct influence on the rate of carbon loss from hummocks than from pools or lawns. The linear correlation coefficient was non-significant for the spot air temperature and CH_4 flux. In Fig. 4.18 the individual site fluxes are shown (cf site water levels in Table 4.5), and it is clear that there was a certain degree of consistency in the rank order of sites with respect to their CH_4 flux, although the order was not the same for each microhabitat, and was not absolute.

The 'annual' mean CH_4-C flux from uncut MH pools, lawns and hummocks was 17, 25 and 8 mg m^{-2} d^{-1}. These values will tend to be overestimates, since they are calculated from data collected during the warmer period of the year.

At CR the methane flux behaved in much the same way, generally, as at MH. There was a five-fold increase in flux between the first records of the year (5 mg m^{-2} d^{-1}, in May) and the peak flux (which occurred in September rather than in August, as at MH) of 25 mg m^{-2} d^{-1}. The 1983 maximum flux was 8 mg m^{-2} d^{-1} more than the 1982 value, and corresponded, like the MH lawn results, to the

relative (MH Met. Off.) air temperature for the two years. Separate analyses for MH and CR (uncut data) gave no significant correlation between the flux of methane and the spot air temperatures recorded in the field.

The overall mean carbon loss as methane from the uncut CR sampling areas was 17.0 mg m^{-2} d^{-1}, compared with 16.8 mg m^{-2} d^{-1} at MH.

No records from uncut areas at either MH or CR indicated a net influx of methane from the enclosed atmosphere into the underlying system.

As already mentioned, the variation in methane flux between sites was greater in summer than at the cooler times of the year, and this trend was more marked at CR (TIME.SITE ANOVA $p<0.001$) than at MH ($p<0.05$). Such a differential seasonal response at the CR sites probably reflects the greater inter-site differences in total peat depth, water régime and exposure, among others, compared with those at MH. At MH each site represented three distinct microhabitat types and therefore each site data set presumably contained a wider spread of flux, water level and temperature régimes, for example, than any CR site, thus reducing the significance of any difference between the MH sites.

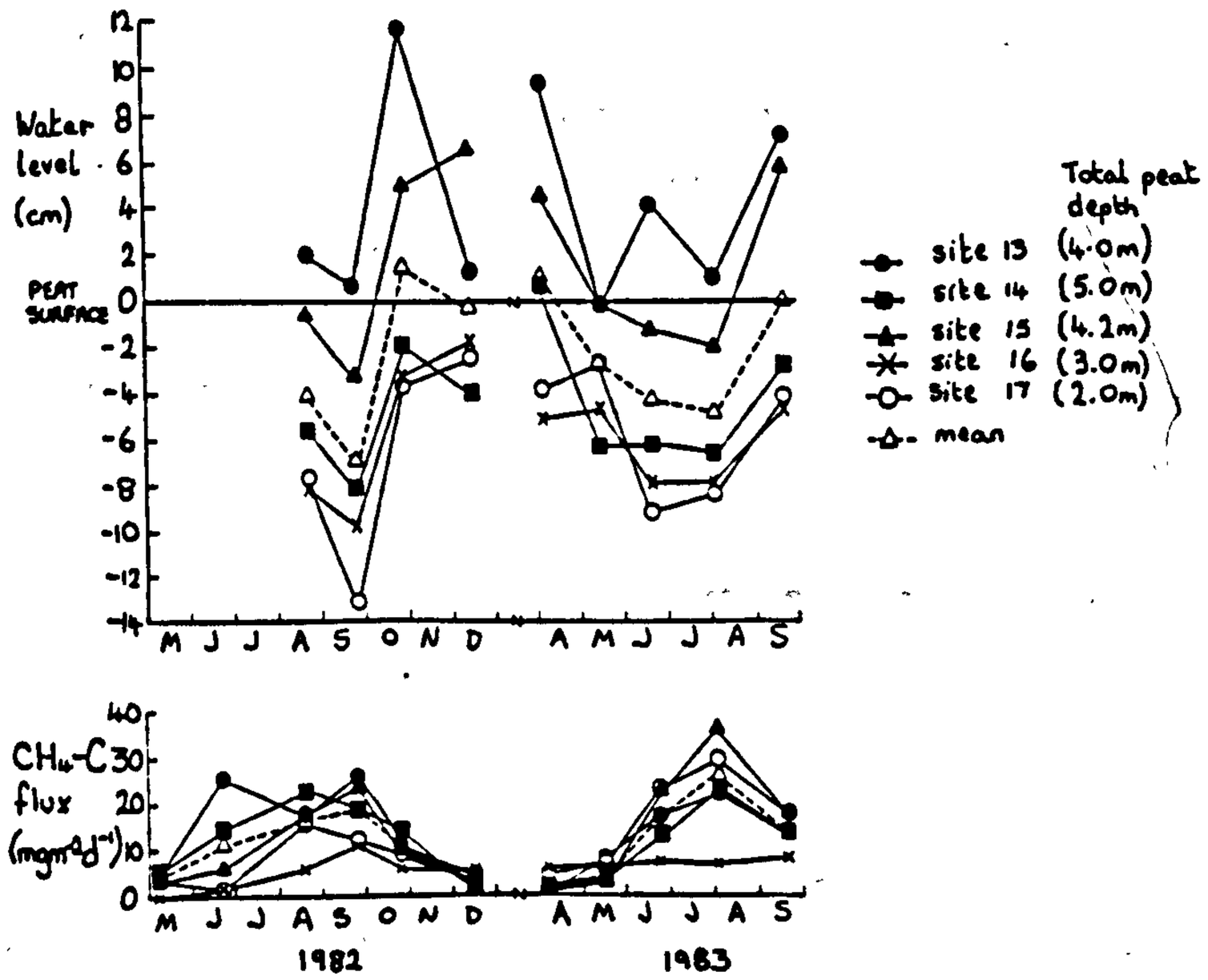
EFFECT OF TOTAL PEAT DEPTH

For convenience, this section deals with CO_2 flux in addition to that of CH_4.

At CR, sampling sites were chosen to represent different total depths of peat (see Table 3.4), reasoning that if decay is occurring over the entire profile this might be reflected in higher fluxes from the surface of deeper peat. An analysis of variance, in which the overall mean gas flux (CH_4 and CO_2 treated separately) at each CR site was tested, returned a highly significant ($p<0.001$) result for the SITE effect, for both components (Table 4.16, p.173). Table 4.13 (p.164), gives the mean site flux for each component and although the sites do not correspond exactly in rank order of peat depth and methane flux, the Table shows clear differences between those sites

with a total peat depth of 4 m or more, and those with 3 m or less. The methane flux was higher over the deeper sites, whereas carbon dioxide efflux was markedly reduced. It may be worth noting that carbon dioxide flux tended to decrease progressively from the peat lagg (site 17) to the site furthest out on the bog (site 13), though the rank order of sites 14 and 15 was interchanged. Fig. 4.19 confirms that this is unlikely to be coincidental, since the same ordering of fluxes and sites was apparent from the individual results of many of the eleven field trips illustrated. It would appear from Fig. 4.20 that the inter-site differences in carbon dioxide flux were more consistent than were the differences in the flux of methane.

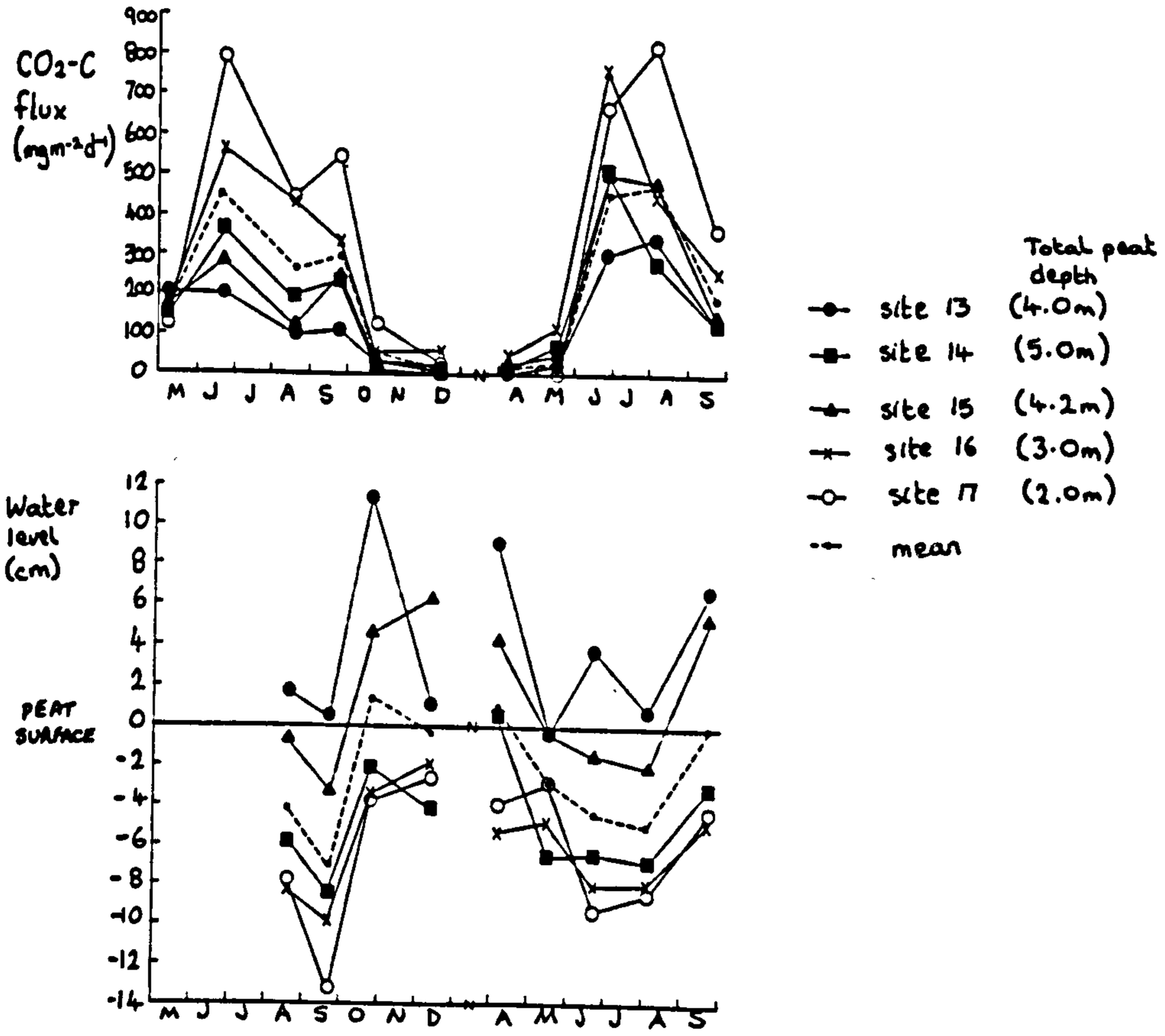
FIG. 4.19 Site differences in water level and surface methane flux, Coom Rigg, 1982-1983. Mean values of 4.



The mean site flux of each gas is a complex measure, representing the net flux resulting from peat processes, those within the photosynthetic biomass, and all interaction between the two. It could be that the observed differences in site fluxes were not the direct result of differences in the extent of the underlying peat decay, but

were produced in some other way, for example by a shift in the relative importance of peat and live-plant processes. The clear sequence of carbon dioxide and oxygen fluxes corresponding to site

FIG. 4.20 Site differences in water level and surface carbon dioxide flux, Coom Rigg, 1982-1983. Mean values of 4.



position could be said to provide support for this interpretation. To help determine which part of the total system is responsible for the differences, the mean site fluxes were re-calculated, separating uncut and cut area results for each site (Table 4.13). The intention here was not to investigate the effect of removing the green matter, that is, not to compare uncut and cut means *within* sites; such a treatment is dealt with in some detail below (Effect of Removing the Green

Matter), but to compare results from uncut and cut cores separately *between* sites. For both uncut and cut site means, the methane flux increased in the same site order as was seen for the overall site mean flux, with the exception of the maximum of the cut area site means seen for site 17. In order of increasing mean methane flux, the cut areas were site 16, site 14, site 15, site 13 and site 17. Carbon dioxide flux from the uncut cores increased in the topographical order of the sites, that is, from the middle of the bog to the lagg.

TABLE 4.13 Selected Coom Rigg surface gas flux statistics.

Factor	Treatment		CH_4-C (mg m^{-2} d^{-1}) Mean	n	Mean	±SE	CO_2-C (mg m^{-2} d^{-1}) Mean	n	Mean	±SE
Site	13 (4,0)*	U	21,9	44	14,8	2,2	137	44	130	37
		C	7,7				123			
	14 (5,0)	U	20,0	39	13,1	2,5	191	39	202	37
		C	5,9				213			
	15 (4,2)	U	20,7	42	13,3	2,4	281	42	195	34
		C	6,9				114			
	16 (3,0)	U	9,7	31	4,7	1,3	445	31	332	79
		C	1,2				250			
	17 (2,0)	U	12,4	38	11,3	3,0	525	38	387	100
		C	10,5				287			
Cut	Uncut			91	17,0	1,6		91	278	42
	Cut			103	6,3	0,8		103	184	24
Grand mean				194	12,1	0,9		194	241	19

* figures in parentheses are total peat depths (m)

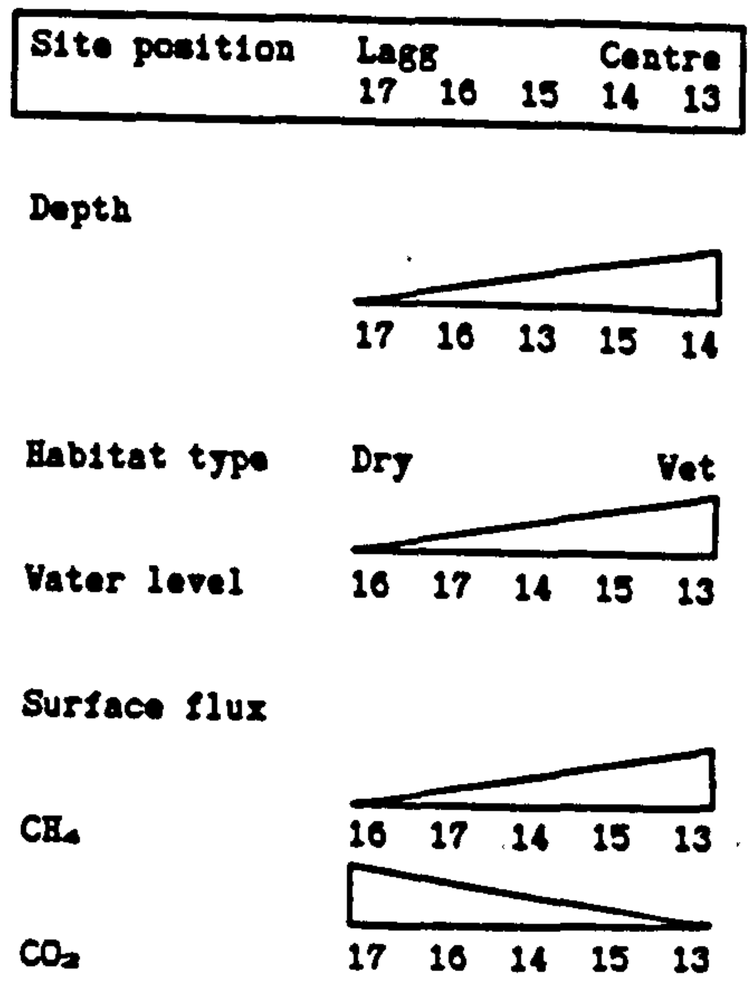
However, when the green matter was removed the sequence was disturbed, and neither corresponded exactly to position on the bog or total peat depth, though it was still the case that the two shallowest sites showed the highest carbon dioxide flux.

In summary, then, there was clearly some correspondence between total peat depth and methane flux, although site 17, the shallowest site and in the lagg, gave unexpectedly high methane flux values. The correspondence was not markedly affected when cut area results were compared, suggesting that at least some of the site differences were

due to the underlying peat system, rather than being due solely to the photosynthetic element of the system or to any differential interaction of the photosynthetic element with a relatively constant underlying system which functions independently of total peat depth. It is not clear from these results what, if any, rôle the photosynthetic biomass plays in the net CH_4 flux. Above the uncut areas, carbon dioxide flux increased from the middle of the bog outwards, and did not appear to correspond very closely with peat depth, and this sequence was generally true for the cut areas, though not precisely so.

Figs. 4.19 and 4.20 clearly illustrate the differences in the flux of each component which led to the significant SITE effect in the analyses of variance (Table 4.16, below). The water level aspect of the SITE effect on gas flux is dealt with in the relevant sections below, but here it may be helpful to include Fig. 4.21 as a summary of overall site differences at CR.

FIG. 4.21 Summary diagram of Coom Rigg differences in site position on the bog, total peat depth, water level and mean gas flux



EFFECT OF THE WATER LEVEL

The effect of the water level on methane flux from the garden cores was assessed a) by comparing fluxes from the cut control cores of pools, lawns and hummocks (i.e. between microhabitats), and b) by comparing fluxes from the uncut experimental cores and uncut control cores of each microhabitat in turn (i.e. within microhabitats). The water levels maintained for each stage are shown in Table 4.3, and are compared with the corresponding CH_4-C flux in Fig. 4.22 (cut controls) and Fig. 4.24 (uncut controls and experimentals).

a) Between microhabitats - garden

Data collected from the cut control cores for stages I-III of the garden experiment (December 1982 to December 1983) were subjected to Wilcoxon matched-pairs (signed-rank) analyses, clumping the data for all stages together to assess the annual effect of different water levels on the gas flux, and then repeating the analyses using data from each stage of the experimemt in turn to determine if water level effects were seasonal. For the purpose of the present analysis (and for that of CO_2 below) any negative CH_4 or CO_2 fluxes were omitted. A summary of the CH_4 results is given in Table 4.14.

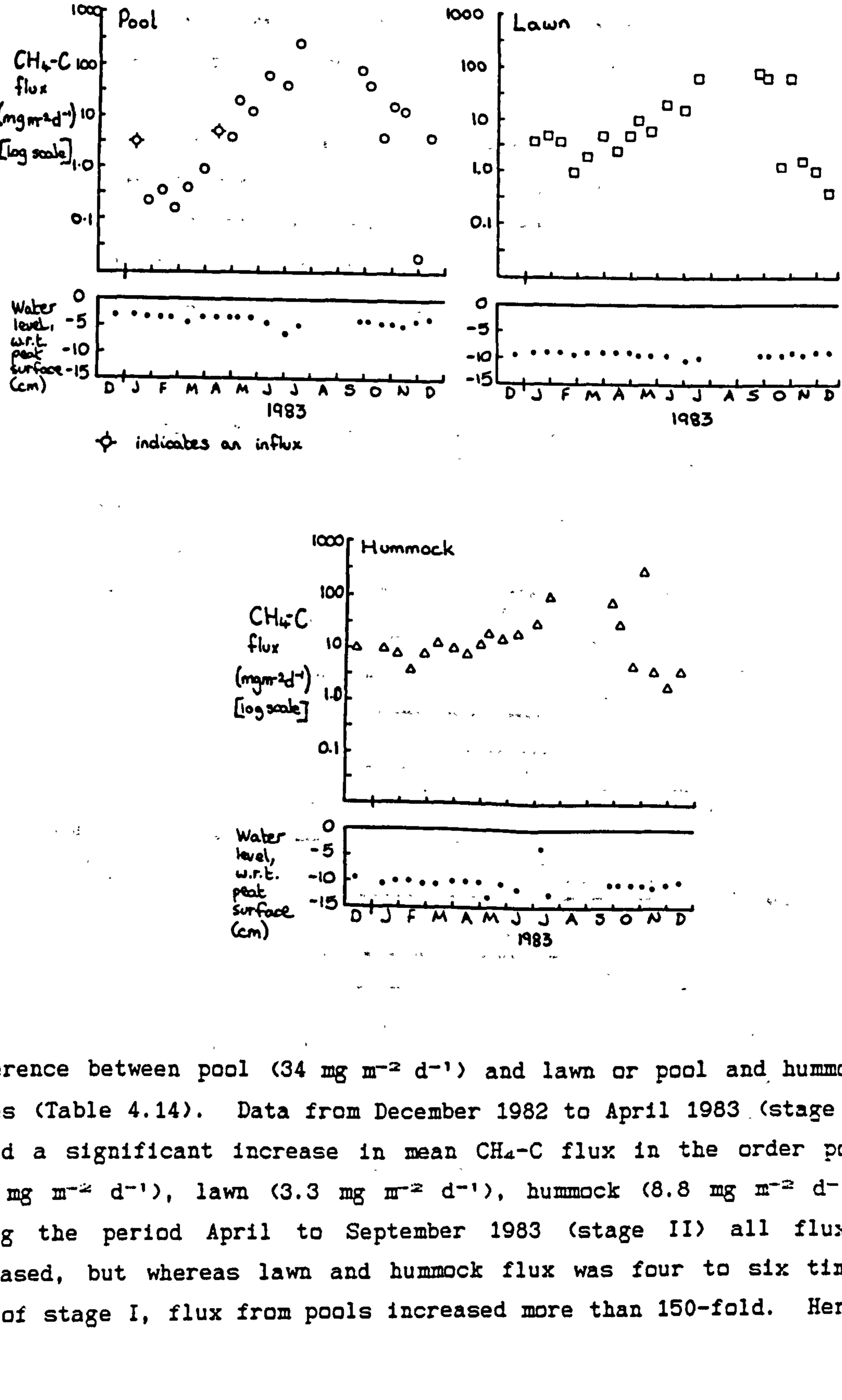
TABLE 4.14 Summary of Wilcoxon matched-pairs analyses, comparing uncut and cut control core methane fluxes (between microhabitats).

Exptal stage	Uncut			Cut		
All	P > L	H > L	P = H	P = L	H > L	P = H
I	P = L	H > L	H > P	L > P	H > L	H > P
II	P = L	H > L	P = H	P > L	H > L	P = H
III	P > L	H > L	P = H	P = L	L = H	P = H

Significant results (i.e. $p<0.05$) shown by >
Non-significant comparisons shown by =

The mean water levels for all stages combined for cut pool, cut lawn and cut hummock controls respectively, were -4.2 cm (nominal), -9.2 cm, and -11.0 cm. Taking all records together ($17 \leq n \leq 20$), the mean CH_4-C flux was greater ($p<0.005$) from hummocks (36 mg m^{-2} d^{-1}) than from lawns (17 mg m^{-2} d^{-1}), but there was no significant

FIG. 4.22 Methane flux from garden cut control cores, December 1982 - December 1983

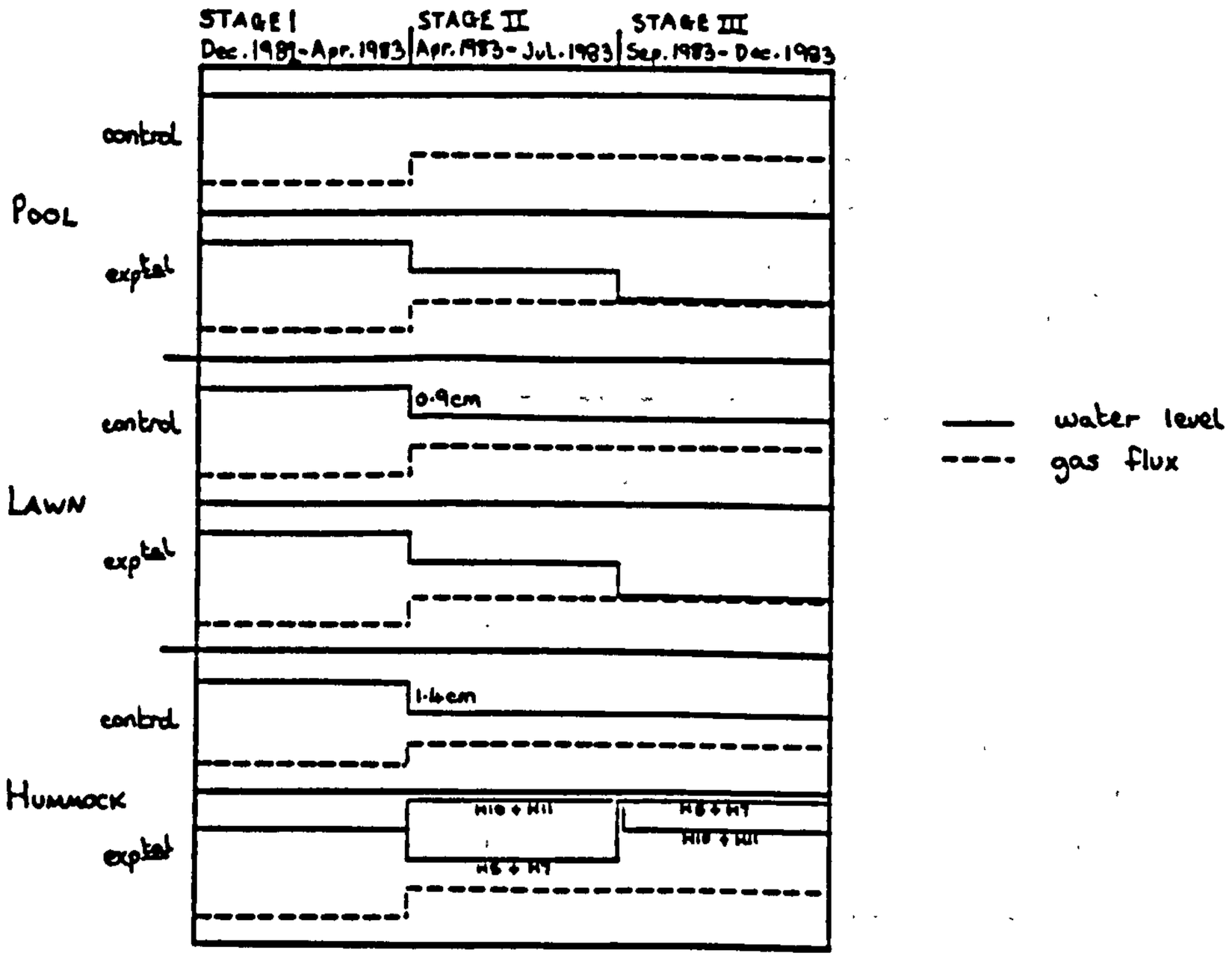


difference between pool (34 mg m^{-2} d^{-1}) and lawn or pool and hummock fluxes (Table 4.14). Data from December 1982 to April 1983 (stage I) showed a significant increase in mean CH_4-C flux in the order pool (0.4 mg m^{-2} d^{-1}), lawn (3.3 mg m^{-2} d^{-1}), hummock (8.8 mg m^{-2} d^{-1}). During the period April to September 1983 (stage II) all fluxes increased, but whereas lawn and hummock flux was four to six times that of stage I, flux from pools increased more than 150-fold. Hence

in stage II the hummock flux remained greater ($p<0.025$) than that of lawns, but was roughly equalled by that of pools. During the period September 1983 to December 1983 (stage III), the mean flux from pools dropped to 26 mg m^{-2} d^{-1}, but the mean values for lawns and hummocks were 29 and 68 mg m^{-2} d^{-1}; higher than those of stage II. However, the fluxes from all microhabitats showed a gradual decline from September to December.

Thus, at the cooler times of the year the mean flux of CH_4-C from each microhabitat increased with increasing dryness of the habitat, that is, P<L<H; but in the warmer periods there was no such correspondence and the efflux from lawns was lower than that from pools and hummocks. Small changes in water level were not mirrored in the CH_4-C flux.

FIG. 4.23 Significant changes in water level and methane flux during the garden experiment. Uncut core data. A step up or down in the horizontal line indicates a significant ($p<0.05$) difference in the mean water level or flux between stages.



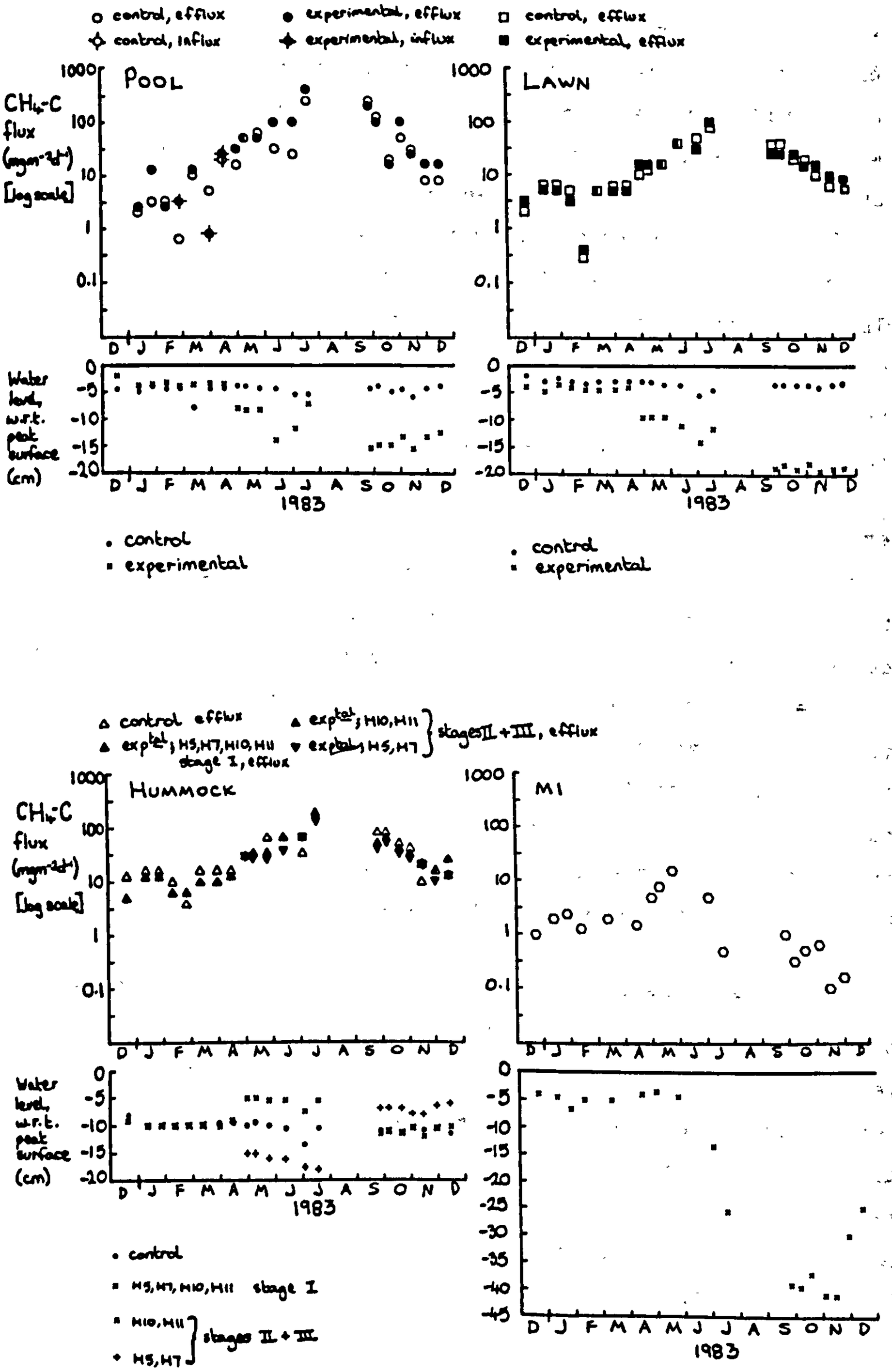
b) Within microhabitats - garden

In order to assess the effect on each microhabitat of a change in water level, data collected from intact (uncut) control and experimental cores and from M1 during stages I to III of the garden experiment were subjected to t-test analyses. Data were paired wherever possible. Fig. 4.24 shows plots of the data sets used, and a summary of the results is given in Fig. 4.23.

Methane flux from all uncut cores - pools, lawns and hummocks; control and experimental - increased significantly I→II ($p<0.05$). This despite control water levels remaining effectively constant throughout (in lawns there was a drop of 0.9 cm I→II and in hummocks a drop of 1.4 cm I→II ($p<0.05$), otherwise non-significant statistical results), and despite significant changes (up or down) in the water level in all microhabitat experimental cores at each stage of the experiment. Further, a significant difference between the water levels in the control cores and those in the experimental cores was maintained for each microhabitat, but differences between the corresponding CH_4-C fluxes were non-significant. The maximum change in water levels imposed during the garden experiment was achieved for the H5 & H7 experimental group in stage III (an increase of +10 cm), but the effect on the flux was insignificant. Hence, it would appear that, for any given microhabitat, water level is not of primary importance in determining the absolute CH_4-C flux, but that temperature is the overriding influence.

The effect of the water level on surface CH_4 flux from the field peat was assessed by making three comparisons: a) the changes in water level and CH_4 flux above each of the three microhabitats at MH and between field-designated 'wet' and 'dry' sampling areas at CR (between microhabitats), b) the seasonal changes in flux and water level within each microhabitat type at MH (within microhabitats), and c) a comparison between the site mean gas fluxes and water levels at MH and CR (between sites).

FIG. 4.24 Methane flux from garden uncut control and uncut experimental cores, December 1982 - December 1983. Mean values.



c) Between microhabitats - field

As for the analysis of the garden data, comparisons of water level and flux between microhabitats at MH and CR were made using only those sampling areas from which the green matter had been removed. Fig. 4.25 shows the changes in cut pool, lawn and hummock water levels and CH_4-C flux at MH. They should only be taken as general trends, since the HABITAT.SITE interaction returned a significant result in analyses of variance for water level ($p<0.01$) and CH_4-C flux ($p<0.001$) (Tables 4.4, above, and 4.15, respectively).

FIG. 4.25 Water level and methane flux changes (cut sampling areas), Moor House, 1982-1983

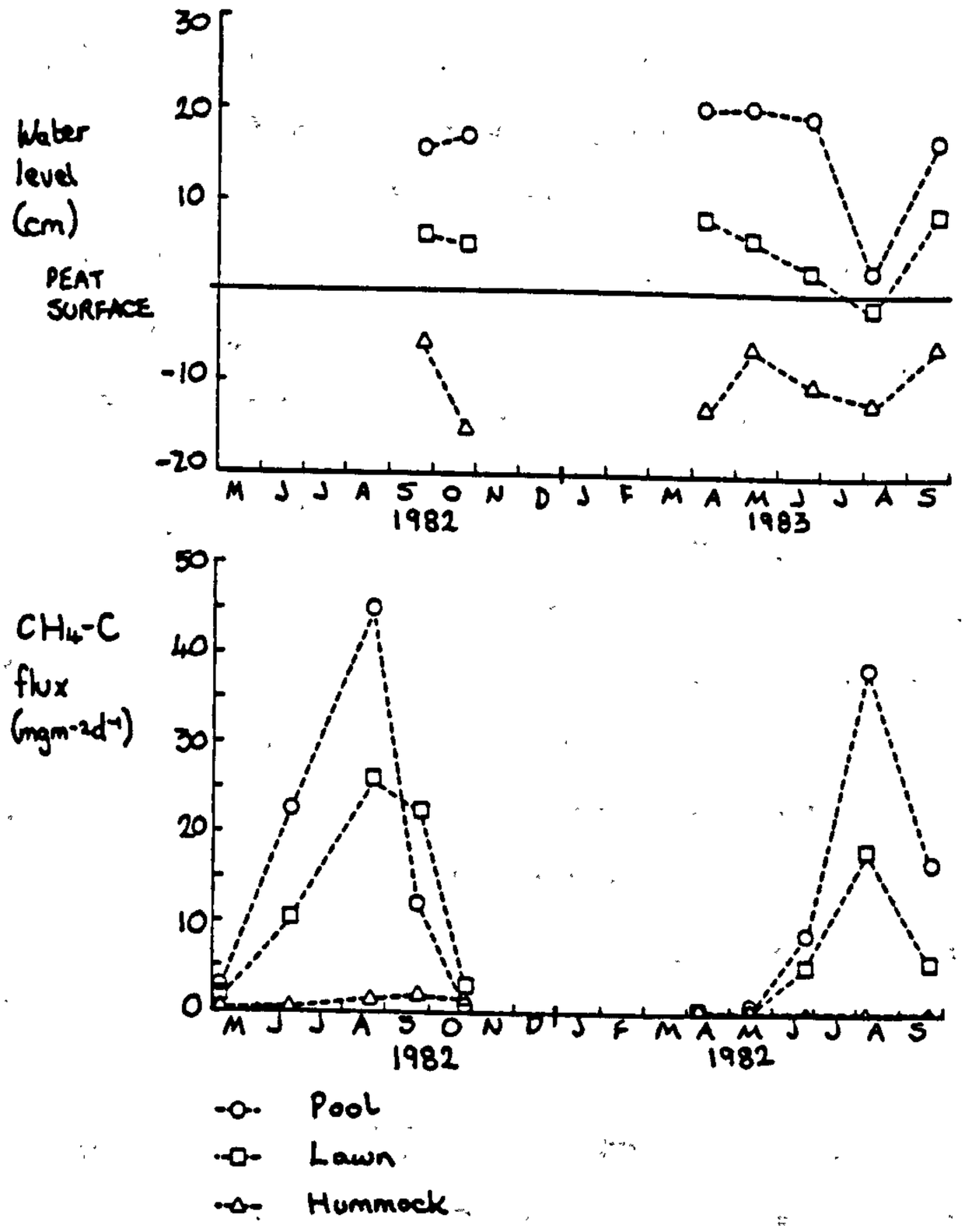


TABLE 4.15 Summary of ANOVA results, Moor House surface gas flux.

Treatment	CH_4	CO_2
TIME	***	***
HABITAT	***	***
CUT	***	NS
TIME.HABITAT	NS	***
TIME.CUT	NS	*
HABITAT.CUT	NS	**
TIME.HAB.CUT	NS	NS
SITE	***	***
TIME.SITE	*	NS
HABITAT.SITE	***	NS
CUT.SITE	NS	NS

The mean water levels (±SE) from the seven sets of MH records made during the period over which the gas samples were collected were 10.7 ±1.3 cm, 0.4 ±0.7 cm and -14.1 ±1.2 cm for CP, CL and CH, respectively, and the differences were significant at the $p<0.001$ level (Fig. 4.25). These corresponded to CP, CL and CH mean CH_4-C fluxes (±SE) of 14.9 ±3.8 mg m^{-2} d^{-1}, 9.5 ±2.7 mg m^{-2} d^{-1} and 0.6 ±0.2 mg m^{-2} d^{-1} (all $p<0.001$). Thus, the roughly 5 mg m^{-2} d^{-1} decrease in mean CH_4-C flux from CP to CL corresponded with a 10 cm drop in water level and the CL to CH decrease in flux of 9 mg m^{-2} d^{-1} was associated with a 14.5 cm drop in mean water level.

At CR there were clear distinctions between the subjectively assigned 'wet' and 'dry' pairs of buckets within the sites, and at sites 14 and 16 these perceived water level differences were statistically sound. For the present analysis, therefore, data from the cut sampling areas at these two CR sites have been used. Water level and methane flux are shown in Fig. 4.26. As at MH, the SITE effect on water level and gas flux was significant ($p<0.001$; Tables 4.6, above, and 4.16).

The mean water levels at CR were -14.0 ±1.5 cm and -6.2 ±1.9 cm for CD and CW areas at site 14, and -7.1 ±1.2 cm and 2.9 ±2.0 cm for CD and CW areas at site 16. The difference in CH_4-C flux between the wet and dry areas at each site was 1 mg m^{-2} d^{-1}, and there was no consistency as to which habitat type showed the highest flux; both site 14 areas had higher mean fluxes than those at site 16 (6.5 ±1.9

mg m^{-2} d^{-1} (CD) and 5.5 ±1.7 mg m^{-2} d^{-1} (CW) for site 14; 0.6 ±0.3 mg m^{-2} d^{-1} (CD) and 1.5 mg m^{-2} d^{-1} (CW) for site 16; Fig. 4.26). Neither was there consistency in the relative CH_4-C flux from the wet and dry

FIG. 4.26 Water level and methane flux in selected cut sampling areas, Coom Rigg, 1982-1983. Individual area data.

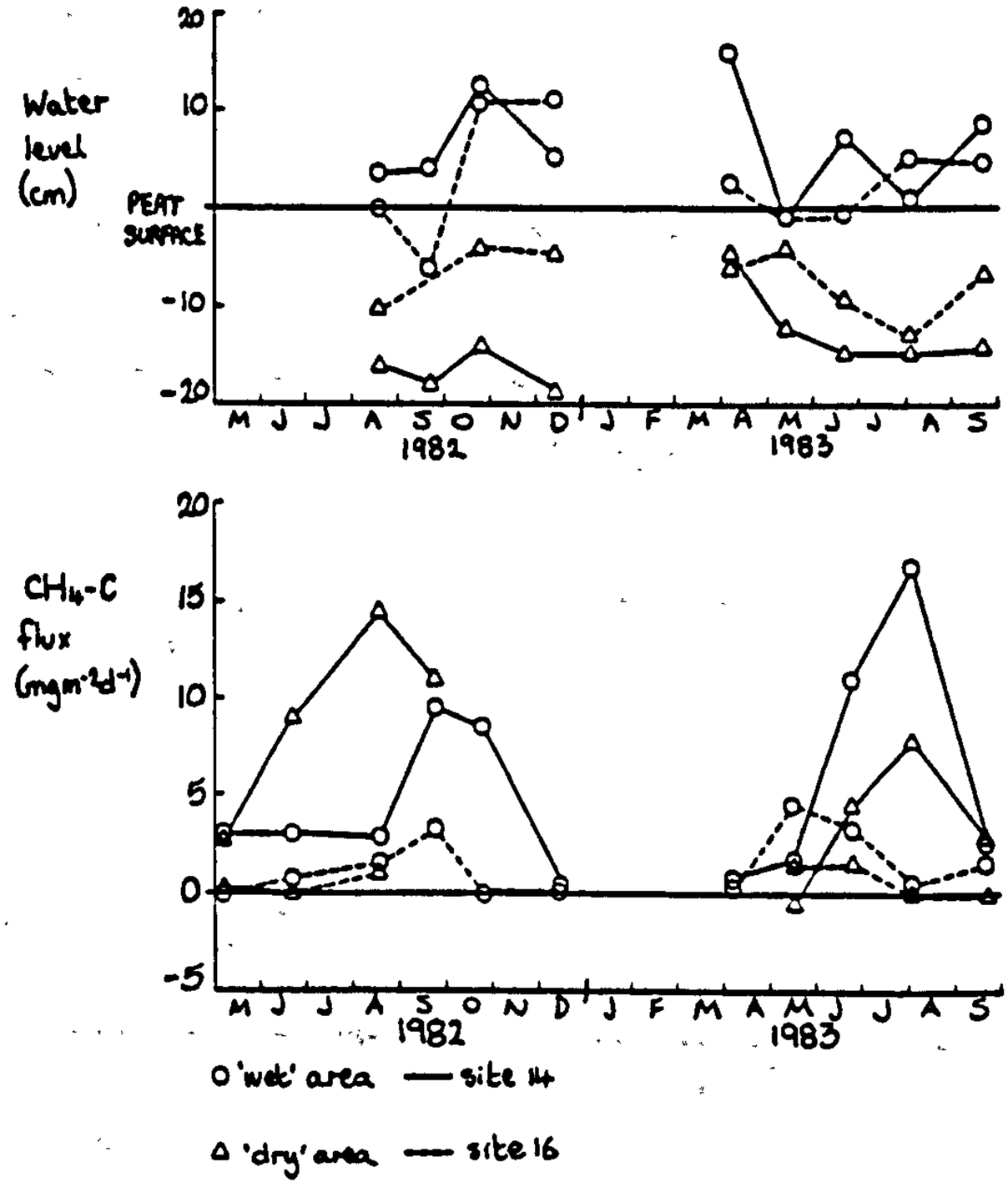


TABLE 4.16 Summary of ANOVA results, Coom Rigg surface gas flux.

Treatment	CH_4	CO_2
TIME	***	***
CUT	***	***
SITE	***	***
TIME.CUT	***	***
TIME.SITE	***	***
CUT.SITE	***	***

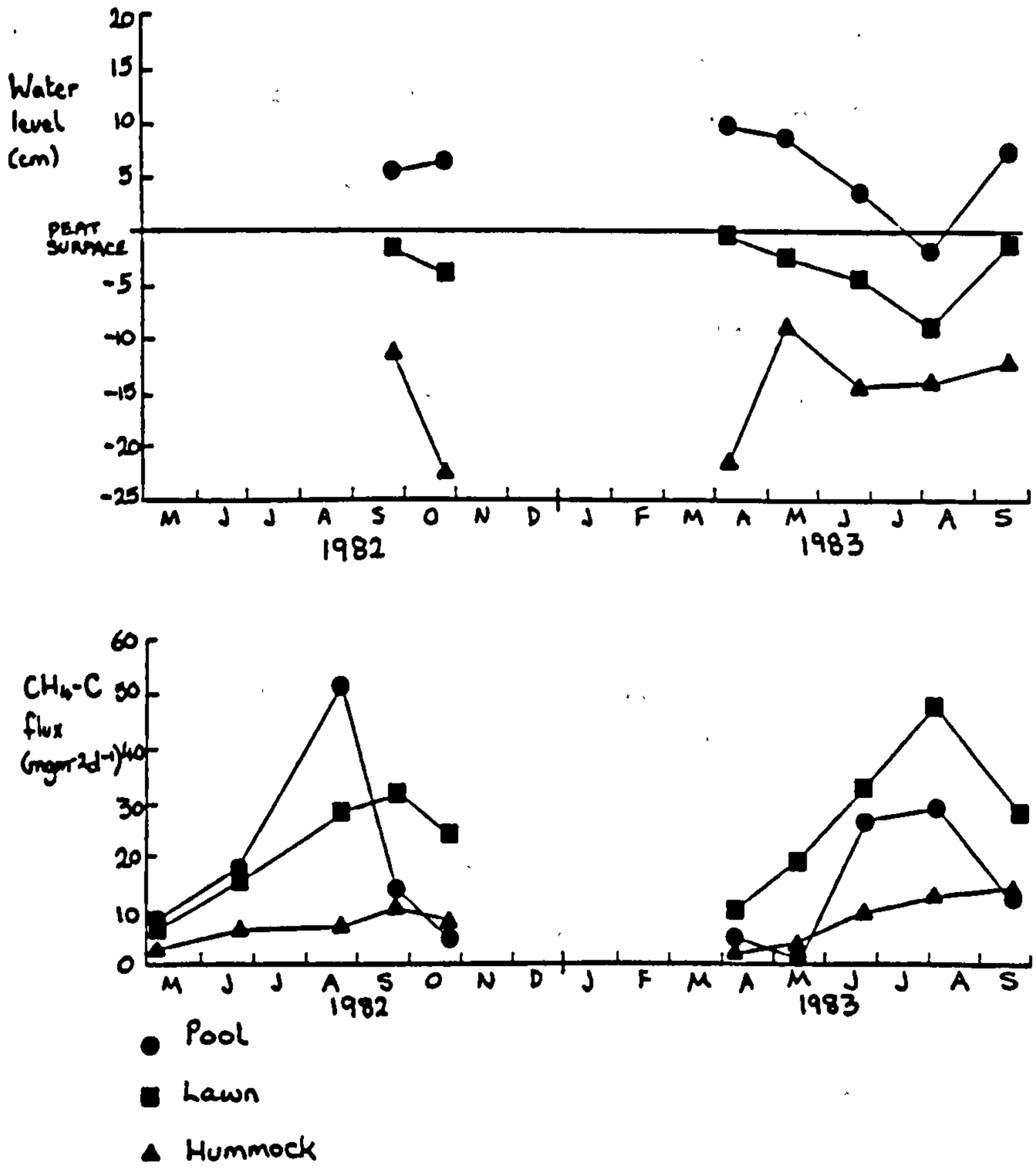
areas of site 14 for the two study seasons, though at site 16 the wet areas showed a higher flux in both years. A possible explanation of these results may be that a small effect of water level on CH_4-C flux is swamped by the inter-site differences in other peat characteristics, such as total peat depth.

d) Within microhabitats - field

The present section is concerned with the effect of the (seasonal) water level changes on each microhabitat type. Data from uncut sampling areas were used.

The relevant parts of Figs 4.14 and 4.18 have been reproduced in Fig. 4.27 to facilitate comparison of water level and methane flux trends. The Figure shows no consistent association between CH_4-C flux and water level in any of the microhabitats at MH.

FIG. 4.27 Water level and methane flux changes, Moor House (uncut sampling areas), 1982-1983. Mean values of 3.



A summary of the coefficients of determination, r^2, obtained from linear regression analyses of methane flux on water level at MH, for uncut sampling areas only, is given in Table 4.17. Results for CO_2 are included for comparison. Seasonal effects are disregarded in this analysis, and the overall correlation between water level and CH_4-C flux is very low, and non-significant, for pools, and for the complete (uncut) MH data set together.

TABLE 4.17 Summary of r^2 values from linear regression analyses of surface flux on water level, Moor House. Uncut data only.

Data set	(n)	CH_4		CO_2	
		r^2	sig.	r^2	sig.
Pool	(28)	0.06	ns	0.25	**
Lawn	(30)	-		0.30	**
Hummock	(29)	-		-	
MH	(87)	0.02	ns	0.35	***
MH & CR	(164)	0.02	ns	0.28	**

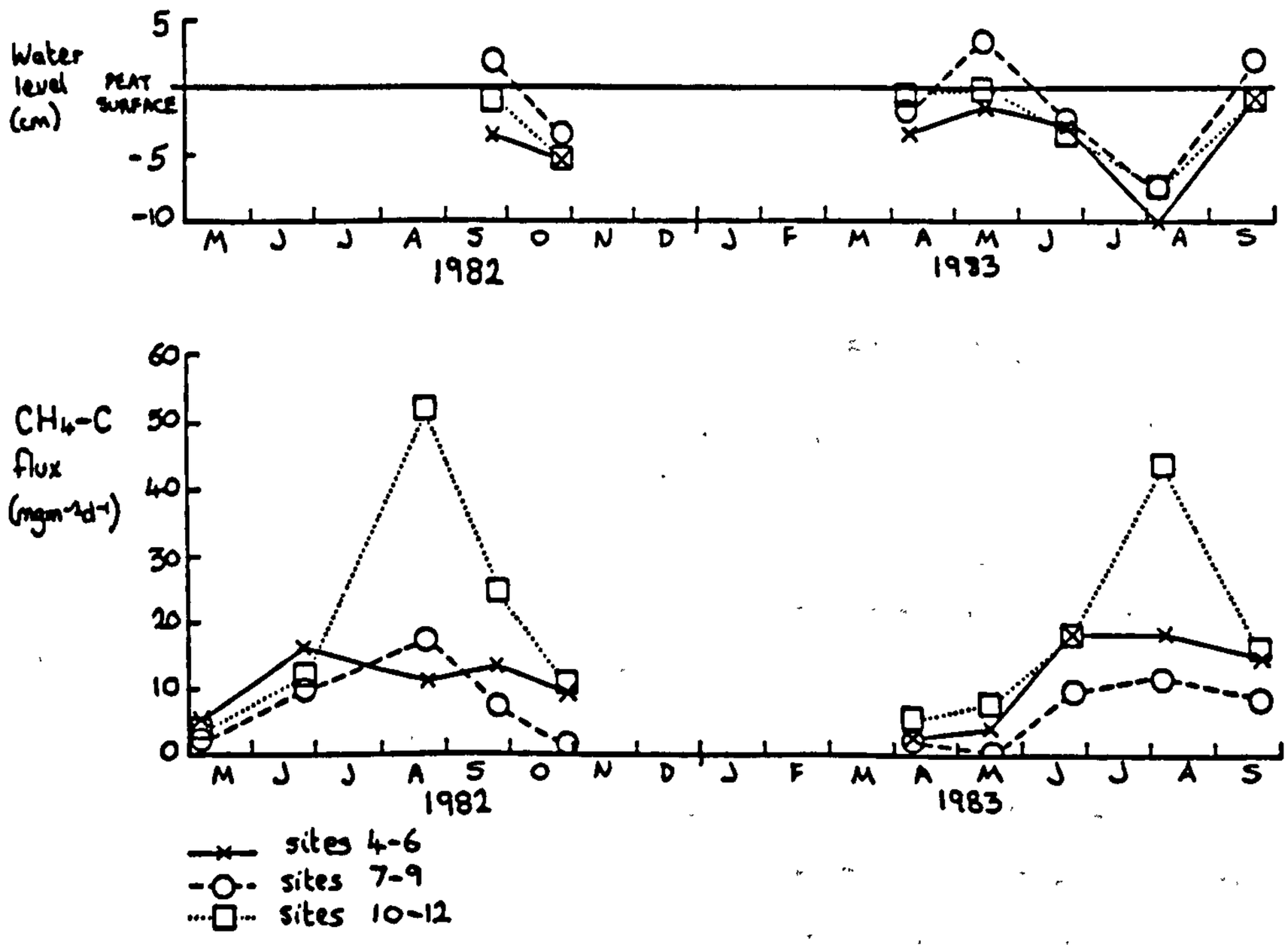
- indicates residual variance > variance of the gas flux variate

Thus these results are not consistent with any one simple explanation of the effect of water level on gas flux. As was suggested by the garden results, when the gross effect of the microhabitat water level difference is removed, the more detailed behaviour of gas flux from a single microhabitat is more difficult to explain, and water level appears to be of no significance, or at most very little. The results under discussion reaffirm this. They are roughly consistent with the idea that peat temperature is most important in the rate of methane production, and that air temperature and water level interact in their effect on its diffusion upwards and out. If such a hypothesis is correct, any more than a gross correspondence between water level and CH_4-C flux would not be expected. The relative importance of temperature and water level effects is considered in more detail below.

e) Between sites - field

Analyses of variance, carried out separately on data from MH and CR using mean site values, regardless of cutting or microhabitat types involved, returned highly significant results ($p<0.001$, Tables 4.4, 4.6, 4.15 and 4.16) for water levels and for CH_4-C flux at both Sites. The effect of SITE on gas flux, with respect to water level differences, is described in this Section for the three MH sites. The SITE effect at CR with respect to total peat depth has been discussed separately, above; the SITE water level effect is included below.

FIG. 4.28 Site differences in water level and surface methane flux, Moor House, 1982-1983. Mean values of 6.



The mean site water levels at MH were -4.6 cm, -0.7 cm and -2.4 cm for sites 4-6, 7-9 and 10-12, respectively. Fig. 4.28 shows the changes in methane flux at each site (uncut and cut; pool, lawn and hummock data clumped for each visit). It is clear that the three sites behaved differently in terms of their methane flux: site 7-9,

the wettest, showed consistently lower CH_4-C fluxes (mean 7.0 mg m^{-2} d^{-1}) than site 4-6, the driest (mean 11.3 mg m^{-2} d^{-1}). Site 10-12, intermediate in terms of water level régime, gave similar results to the other sites up to about May of each season, but its peak in methane flux in August was two-and-a-half- to three-fold that of the other two sites (mean 19.4 mg m^{-2} d^{-1}).

A comparison of the water level and methane flux plots for each site in Fig. 4.28 reveals the same overall lack of direct correspondence between the two in the summer but the suggestion of a stronger water level correspondence at the cooler ends of the season.

The individual microhabitats behaved differently in terms of both their water level ($p<0.01$) and methane flux ($p<0.001$) at the three MH sites, according to the results of two analyses of variance to test the HABITAT.SITE interactive effect. The range of mean CH_4-C fluxes over the three sites was largest for lawns (31 mg m^{-2} d^{-1}), compared with 4 mg m^{-2} d^{-1} and 6 mg m^{-2} d^{-1} for hummocks and pools, respectively. This is in contrast to the mean water levels, which showed the smallest range for lawns and the largest for hummocks. Thus, lawns appear to contribute most to the (significant) difference between site microhabitat fluxes, despite relatively stable water levels.

TABLE 4.18 Summary of r^2 values from linear regression analyses of surface gas flux on water level, Coom Rigg. Uncut data only.

Data set	(n)	CH_4 r^2	sig.	CO_2 r^2	sig.
Site 13	(20)	-		-	
Site 14	(18)	-		0.47	**
Site 15	(16)	-		0.52	**
Site 16	(11)	0.35	ns	-	
Site 17	(12)	-		0.19	ns
CR	(77)	0.02	ns	0.28	**
MH & CR	(164)	0.02	ns	0.28	**

- indicates residual variance > variance of the gas flux variate

At CR, the rank order of increasing wetness was site 16 (mean water level -5.5 cm), 17 (-5.1 cm), 14 (-4.0 cm), 15 (2.0 cm) and 13 (4.0 cm); see Table 4.7 and Fig. 4.15. The overall site mean CH_4-C flux increased in the same order: site 16 (4.7 mg m^{-2} d^{-1}), 17 (11.3 mg m^{-2} d^{-1}), 14 (13.1 mg m^{-2} d^{-1}), 15 (13.3 mg m^{-2} d^{-1}) and 13 (14.8 mg m^{-2} d^{-1}); see Table 4.13 and Fig. 4.19. These are the mean values, and there is variation in the rank order of sites in terms of their mean water level and methane flux, between visits. It should also be remembered that the sites at CR differed considerably in their total peat depth (Table 3.4), amongst other factors. Table 4.18 shows the r^2 values for the regression of gas flux on water level at the CR sites (uncut data only). The values were non-significant for methane.

RELATIVE IMPORTANCE OF TEMPERATURE AND WATER LEVEL

The results reported above have suggested that temperature, and to some degree water level, are correlated with methane flux, but the relative importance of these factors in each microhabitat is less clear. The comparison of time curves suggests complex interactions which make generalisation difficult. To investigate in more detail and to clarify any such associations, the variables listed in Table 4.19 were used as the independent variables in a series of linear

TABLE 4.19 Independent variables used in garden gas flux vs temperature and water level regression analyses.

Label	Description
x_1	Median peat-air interface temperature for the two-day sampling period (°C)
x_2	Calculated temperature of the peat at -30 cm at the time of sampling, based on the appropriate air-peat regression equation calculated previously, and the air temperature at sampling (°C)
x_3	Calculated mean peat temperature at -30 cm for the period since the last gas samples were taken, based on the appropriate interface-peat regression equation and using the interface temperatures measured in M2 (°C)
x_4	Water level relative to the peat surface, assuming no peat growth between measurements (cm)
x_5	Water level relative to the peat surface, assuming constant peat growth between measurements (cm)
x_6	Air temperature (+1.5 m) at the time of sampling (°C)

regression analyses on the garden data. Methane flux data (CH_4-C, mg m^{-2} d^{-1}) collected between May 1981 and December 1983 (stages Pre I to III) from intact cores provided the dependent variables. Analyses were carried out using each independent variable individually to determine the relative importance of temperature and water level effects on the flux from each microhabitat, at different times of the year. To this end, three sets of analyses were carried out for each microhabitat; the first included all data ($100 \leq n \leq 126$ pairs), the second all data collected when the air temperature was below 10°C (approximately the annual mean temperature) ($n \simeq 50$ pairs), and the third all data collected when the air temperature was 10°C or more ($n \simeq 50$ pairs). The results are summarised in Table 4.20, in which those for CO_2 are also given, for comparison. Variables x_2 and x_5 have been omitted from the Table because they contribute very little; x_2 is not independent of x_5, and x_5 was found to give consistently low r^2 values.

It is well known that temperature and water level effects do not act independently (e.g. Douglas & Tedrow 1959; Flanagan & Veum 1974; Heal & French 1974), so the same independent variables were then used simultaneously in multiple regression analyses to investigate their interactive effect on CH_4-C flux. The multiple correlation coefficients were maximised for variables of the first order only, to facilitate interpretation of the final equation. This does not necessarily represent the best-fit line, because as variables are added the F-value usually decreases. The results are summarised in Appendix Ka.

It is clear from Table 4.20 and Appendix Ka that methane flux is primarily correlated with temperature, and that water level is of secondary, if any, significance. The absolute importance of water level, and that relative to temperature, varies with microhabitat and season. Overall, temperature accounts for between 63% and 82% of the variation in methane flux, whilst water level accounts for a maximum of 20% (in hummocks). At cooler times of the year (air temperature <10°C) the degree of correlation between CH_4-C flux and temperature falls by 10% or more. It remains the most important factor for lawns and hummocks (r^2=0.74 and 0.64, respectively), but in pools water

TABLE 4.20 Summary of results from linear regression analyses of temperature and water level on gas flux from uncut garden peat cores. Individual variable r^2 values. Signs indicate those of r, the correlation coefficient. A full description of the variables is given in Table 4.19.

	Uncut pool		Uncut lawn		Uncut hummock		Mi		Mean air temp.		
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	(°C)	n	Data set
All records											
x_1 Med. interface 2d temp.	0.66	0.25	0.76	0.57	0.76	0.76	0.22	0.10	10.3	30	All
x_2 Air temp. at record (sampling)	0.63	0.08	0.72	0.45	0.71	0.69	0.29	0.06			
x_3 Calculated mean peat temp. since last sampling	0.64	0.20	0.82	0.54	0.79	0.70	0.29	0.05			
x_4 Water level (no growth)	-0.11	-0.49	-0.08	-0.54	-0.19	-0.25	0.28	0.37			
<10 °C											
x_1 Med. interface 2d temp.	-0.05	0.12	0.19	0.07	0.22	0.01	0.24	0.26	10.5	12	PRE I
x_2 Air temp. at record (sampling)	-0.11	-0.32	0.03	-0.16	-0.03	0.06	0.15	0.14			
x_3 Calculated mean peat temp. since last sampling	0.24	0.38	0.74	0.43	0.64	0.12	0.45	0.24			
x_4 Water level (no growth)	-0.48	-0.72	-0.49	-0.71	0.07	0.08	-0.21	-0.27			
>10 °C											
x_1 Med. interface 2d temp.	0.60	0.04	0.75	0.45	0.75	0.69	0.82	0.67	5.3	6	I
x_2 Air temp. at record (sampling)	0.55	-0.24	0.70	0.22	0.70	0.54	0.64	0.44			
x_3 Calculated mean peat temp. since last sampling	0.59	-0.01	0.80	0.41	0.77	0.66	-0.17	-0.08			
x_4 Water level (no growth)	-0.08	-0.53	0.00	-0.71	-0.18	-0.26	-0.76	-0.90			
x_1 Med. interface 2d temp.							-0.58	ns	15.3	5	II
x_2 Air temp. at record (sampling)							-0.17	ns			
x_3 Calculated mean peat temp. since last sampling							-0.61	ns			
x_4 Water level (no growth)							0.70	ns			
x_1 Med. interface 2d temp.							0.69	0.63	7.6	7	III
x_2 Air temp. at record (sampling)							0.83	0.86			
x_3 Calculated mean peat temp. since last sampling							0.56	0.55			
x_4 Water level (no growth)							-0.55	-0.44			

level assumes the greatest importance (r^2=0.48, cf r^2=0.11 for all data). There was very little difference between the (squared) correlation coefficients of the different temperature variables when all data were analysed, but at the cooler times of year the mean calculated peat temperature since the previous sampling assumes much more importance, at the expense of the air temperature at sampling and the two-day median interface temperature. Results from the data representing periods with air temperature at 10°C or above are similar to those when all data were combined, which is not surprising since the significance of the coefficients in Appendix Ka is reduced for the 'cool period' data set. Thus, temperature is most closely correlated

with methane flux from all microhabitats at warmer times ($0.55 \leq r^2 \leq 0.80$), and there is little difference between the individual variable correlation coefficients. At such times the association with water level is negligible (in pools and lawns) but accounts for just less than 20% of the variation in CH_4-C flux from hummocks.

Data from M1 were used to obtain r^2 values for each stage of the garden experiment in turn, irrespective of air temperature. Fewer samples were collected from M1, and data sets consisted of 12, 6, 5 and 7 pairs for the Pre I, I, II and III stage analyses, respectively. The complete set of M1 data (n=30 pairs) was also analysed. The results are included in Table 4.20 and Appendix Ka. The reduced data set sizes are reflected in the lower significance levels of the regression equations and the high r^2 values. In general, the results are therefore less reliable than those from the cores, especially those of stage II ($p<0.30$). They suggest that during stage I (mean air temperature ≈5°C, mean peat temperature at -30 cm = 5°C) the methane flux was about equally associated with the (interface) temperature ($r^2=0.82$) and the water level ($r^2=0.76$). In stage III (mean air temperature ≈8°C, mean peat temperature at -30 cm ≈10°C), 83% of the variation in CH_4-C flux was accounted for by (air) temperature. With the exception of those from stage II, these results are in general agreement with those from the cores, in that the effect of temperature is reduced relative to that of water level during the cooler times of the year.

A similar set of regression analyses was carried out on the field data (uncut areas, collected May 1982 to September 1983), which were analysed together, and as sub-sets, to try and detect any variation in results between microhabitats, sites or both. The independent variables used are listed in Table 4.21. Individual variables were tested first, followed by a stepwise multiple regression approach. Median peat-air interface temperatures were only available from May (two-day median) and June (between-visit median) 1983 onwards, so the inclusion of these variables considerably restricted the number of data items included in any analysis. Hence, each analysis was run

TABLE 4.21 Variables used in multiple regression analyses of surface gas flux at Moor House and Coom Rigg.

y	Gas flux (mg m^{-2} d^{-1} CH_4-C, CO_2-C) (dependent)
x_1	Air temperature (+1.5 m) at time of record (study data) (°C)
x_2	Met. Off. mean monthly maximum air temperature (+1.5 m) (°C)
x_3	Met. Off. monthly minimum air temperature (°C)
x_4	Met. Off. mean monthly temperature (°C) (½(max+min))
x_5	Median peat-air interface temperature (+5 cm) since previous field visit (°C)
x_6	Median peat-air interface temperature for 2-day sampling period (°C)
x_7	Predicted peat temperature at -30 cm at time of record, calculated from sine wave equation based on MH data collected during study: $T_{(z,t)} = 4.8 + 16.0\ e^{-z/40.0}\ \mathrm{Sin}\ ((2\pi t/365.0) - z/40.0)$ (°C)
x_8	As x_7, for period since previous field visit (°C)
x_9	Predicted peat temperature at -30 cm at time of record, calculated from sine wave equation based on 1981 MET data: $T_{(z,t)} = 4.9 + 7.5\ e^{-z/80.0}\ \mathrm{Sin}\ ((2\pi t/365.0) - z/80.0)$ (°C)
x_{10}	As x_9, for period since previous field visit (°C)
x_{11}	Water level, below peat surface, i.e. negative values represent standing water (cm)

firstly without the median interface data (termed 'full' data set) and then with them included (termed 'restricted' data set). Table 4.22 details the size and contents of each data set analysed.

Of the 11 field visits made during this time, air and (predicted) peat temperatures fell below the annual mean of 5°C only once or twice, so there were insufficient data available to be able to investigate the relative importance of temperature and water level effects at times of the year when the temperature was below the annual mean, as was done for the garden data. Results of the analyses reported in the present Section therefore summarise the situation when peat and air temperatures were above 5°C.

Table 4.23 gives an effective summary of the important results. Appendix L gives the full set of results.

Irrespective of which data set was analysed, the influence of the water level on CH_4-C flux was clearly very small; r^2 values varied between 0.01 and 0.35 (Appendix La) and not all of these were significant. Of the four data sets which returned significant ($p<0.05$) r^2 values (UL, UH, CR and MH & CR) water level accounted for only 1-3% of the variation in methane flux. However, when a multiple

regression analysis was carried out, adding temperature variables to the water level data, seven of the eleven data sets showed significant r^2 values ($p<0.05$). Overall, with MH and CR data clumped together, a multiple ('seven-variable') regression involving water level, spot air

TABLE 4.22 Data sets used in multiple regression analyses of surface gas flux at Moor House and Coom Rigg. Uncut sampling areas only.

Data sets	Full data set* n	Restricted data set† n
1. Pool	27	8
2. Lawn	29	8
3. Hummock	28	8
4. MH	86	26
5. Site 13	17	5
6. Site 14	16	5
7. Site 15	14	5
8. Site 16	10	3
9. Site 17	11	4
10. CR	72	26
11. MH & CR	159	53

* without MED2D (x_6) and MEDLAST (x_5)
† with MED2D and MEDLAST

temperature, Met. Off. maximum, minimum and mean air temperatures and the predicted peat temperatures at -30 cm based on the MH sine wave equation for the time of the record and the period since the previous field visit, accounted for 27% of the variation in methane flux (Table 4.23). Substituting in the predicted peat temperatures based on the Met. Off. sine wave equation for those based on MH data effected no change in the value of r^2 or its significance ($p<0.001$).

At CR the seven variables listed above accounted for 57% of the variation in methane flux ($p<0.001$), while at MH they accounted for only 18% ($p<0.05$). At MH only the UP data set gave a significant r^2 value for this same multiple regression (0.54, $p<0.05$): the lawns and hummocks gave r^2 values of 0.42 and 0.41, respectively, but were not significant. Individually, the Met. Off. maximum, minimum and mean temperatures accounted for 25%, 27% and 28% of the variation in methane flux from the MH pools, the only significant variables

TABLE 4.23 Summary of multiple linear regression analyses of gas flux on temperature and water level at Moor House and Coom Rigg. Uncut area data only. Variables and units listed in Table 4.21. Coefficients of determination for linear regressions, and significance of regressions.

	Variables											Data set (full)																	
	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	UP		UL		UH		MH		site 13		site 14		site 15		site 16		site 17		CR		MH&CR	
												r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.
CH_4	+	+	+	+			+	+			+	0.54	*	0.42	ns	0.41	ns	0.18	*	0.71	*	0.91	***	0.80	*	0.81	ns	0.67	ns	0.57	***	0.27	***
	+	+	+	+					+	+	+	0.53	*	0.42	ns	0.41	ns	0.18	*	0.71	*	0.91	***	0.79	*	0.89	ns	0.67	ns	0.57	***	0.27	***
											+	0.06	ns	-		-		0.02	ns	-		-		-		0.35	ns	-		0.02	ns	0.02	ns
CO_2	+	+	+	+			+	+			+	0.40	ns	0.70	***	0.54	*	0.50	***	0.63	ns	0.60	ns	0.85	*	0.93	ns	0.97	**	0.53	***	0.44	***
	+	+	+	+					+	+	+	0.78	ns	0.69	***	0.53	*	0.50	***	0.62	ns	0.60	ns	0.84	*	-		0.97	**	0.53	***	0.44	***
											+	0.25	**	0.30	**	-		0.35	***	-		0.47	**	0.52	**	-		0.19	ns	0.28	**	0.28	**

- indicates residual variance > variance of gas flux

($p<0.05$) of the seven involved in this regression. Thus it appeared that in the pools water level was not an important influence, but that the monthly mean temperatures were. Also, since the r^2 values for these three variables were so similar, the multiple regression would be little affected if only one of the three were included in it. Interestingly, sites 13, 14 and 15 (the three wettest CR sites) also returned significant r^2 values for the seven-variable multiple regression under discussion. The data sets involved were only about half the size of the UP data set ($14 \leq n \leq 17$, cf $n=27$ for UP), but the linear regression accounted for 71% ($p<0.05$), 91% ($p<0.001$) and 80% ($p<0.01$) of the variation in methane flux at sites 13, 14 and 15, respectively.

In summary, it would appear that gross differences in the water level (such as those between the three different microhabitats at MH) play a significant rôle in influencing the methane flux from peat (e.g. Fig. 4.18, Table 4.15, above) but smaller fluctuations are not directly associated with the small-scale gas flux changes (during the times of the year when the temperature of peat and air is at or above the annual mean). At these warmer times of year, the temperature accounts for more of the variation than does the water level, within each microhabitat. It is possible that when temperatures are lower they become limiting and the effect of water level on methane efflux (not necessarily ≡ production) is more pronounced (as suggested by the results described above, Section 4.2.4, Effect of the Water Level on Methane Flux in the Field (Within Microhabitats).

Temperature effects were apparently more significant the wetter the habitat, in the warmer periods of the year, and in these areas, of the seven variables, the monthly mean, maximum and minimum air temperatures were most closely correlated. Information on water level, monthly mean air temperature and, possibly, temperature of peat at about -30 cm would reasonably describe the methane flux changes at least as well as is possible from the full set of variables involved here.

RELATIONSHIP BETWEEN METHANE FLUX AND PEAT SULPHIDE

Water level, depth of sulphide zone (taken as the uppermost depth at which discolouration was continuous over at least half the width of the strip), and methane flux data from MH and CR were subjected to linear regression analyses to determine whether or not the surface methane flux could be predicted from changes in the sulphide zone depth, or that and the water level. Nine analyses were carried out in each case. The data sets used and the results are shown in Table 4.24.

TABLE 4.24 Summary of results from regression analyses of methane flux and sulphide zone depth at Moor House (all sites) and Coom Rigg (sites 13, 14 and 16 only). Uncut sampling areas only.

CH_4 on S^{2-}			CH_4 on S^{2-} and water level		
Data set	r^2	Sig. level	Data set	r^2	Sig. level
Pool	-	ns	Pool	-	ns
Lawn	0.08	ns	Lawn	0.00	ns
Hummock	0.13	ns	Hummock	0.16	ns
MH	0.07	*	MH	0.07	ns
Site 13	0.53	*	Site 13	0.53	ns
Site 14	-	ns	Site 14	-	ns
Site 16	-	ns	Site 16	-	ns
CR	0.36	**	CR	0.41	**
MH & CR	0.10	**	MH & CR	0.10	**

There was no significant correlation between methane flux and the depth of the sulphide zone at any of the microhabitats at MH, although when pooled, MH data showed a significant correlation ($p<0.05$), but only 7% of the variation in flux was accounted for. Inclusion of the water level had no effect. The pooled CR data gave $r^2=0.36$ ($p<0.01$). When water level was included in the individual CR site analyses no significant results were returned, but the pooled CR data r^2 value improved slightly to 0.41 ($p<0.01$). Thus at CR an upward movement in the sulphide zone was associated with an increase in methane flux at the surface. At MH the pooled data showed a weak association, but none for individual microhabitats. Only 10% of the methane flux

variation in the complete MH and CR data set could be explained in terms of the movement of the sulphide zone ($p<0.01$), whether or not water level was included in the analysis.

EFFECT OF REMOVING THE GREEN MATTER

At the end of November 1982 the green matter was removed from half the peat cores in the garden plot. The mean dry weight removed from pool, lawn and hummock cores at that initial sampling was 5, 39 and 40 g, respectively.

Data collected from the cut cores were subjected to the same analyses as described for the intact cores. In addition, where appropriate, direct statistical comparisons between uncut and cut core fluxes were made. The results for methane are described in the present section. They are complicated, so that generalisations are difficult and in most cases exceptions can be found. However, a few consistent effects did appear to emerge, and these are summarised here.

a) Seasonal change

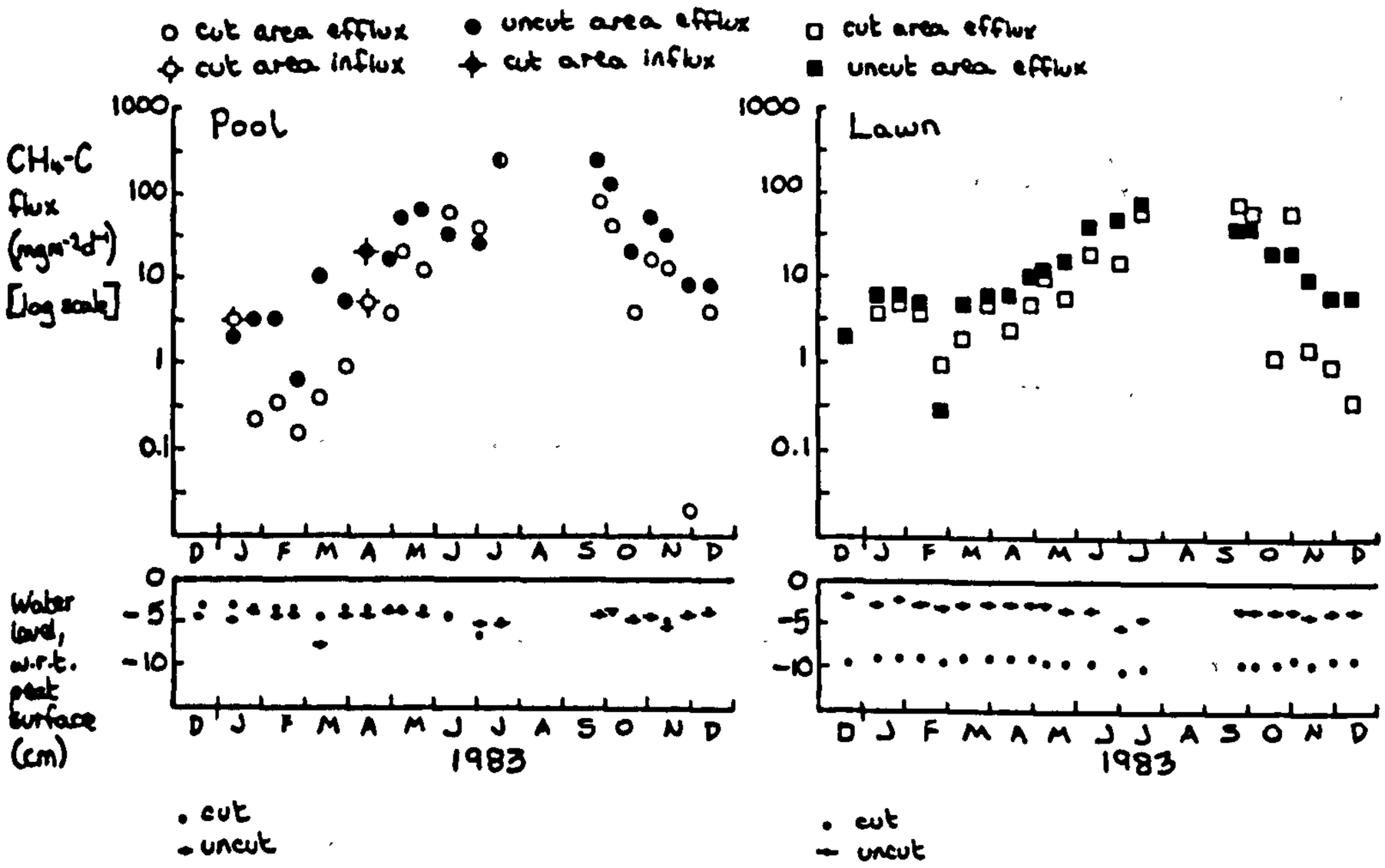
In general, there was no difference in the seasonal pattern of methane efflux from uncut and cut cores; the peaks and troughs coincided (Fig. 4.29). However, the absolute flux values differed, slightly though significantly, there being more CH_4-C lost from the intact cores than from the cut ones, and the difference was largest above pools (Table 4.25). Above lawns and hummocks the difference was

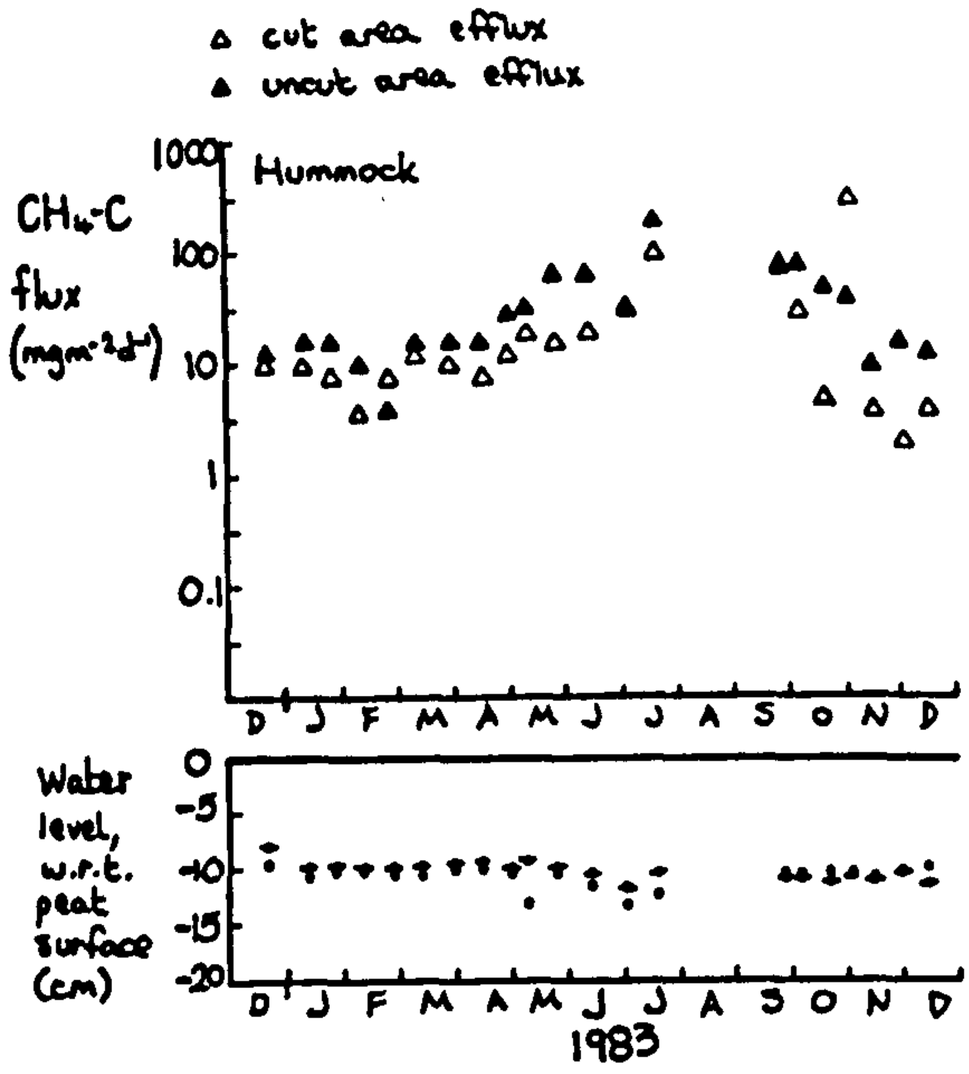
TABLE 4.25 Summary of methane fluxes from uncut and cut control cores. Mean flux for period shown.

Exp^{tal} Stage	Pool		Lawn		Hummock	
	Uncut	Cut	Uncut	Cut	Uncut	Cut
	(mg m^{-2} d^{-1} CH_4-C)		(mg m^{-2} d^{-1} CH_4-C)		(mg m^{-2} d^{-1} CH_4-C)	
All*	49	34	18	17	37	36
I	4	0.4	5	3	13	9
II	70	70	35	19	66	34
III	69	26	19	29	39	68

* mean of stages I-III

FIG. 4.29 Comparison of surface methane flux from uncut and cut control cores





very small. Using individual sample data, the Wilcoxon matched-pairs test was applied to assess the significance of any observed differences between uncut and cut cores. The results of these analyses are shown in Table 4.26. Approximately 20 pairs of data were involved in comparisons of all stages together, whereas n varied between 5 and 8 for individual stage comparisons. The rate of change of CH_4-C flux at the beginning and end of the season was different

TABLE 4.26 Summary of Wilcoxon matched-pairs analyses, comparing uncut and cut control core methane fluxes (within microhabitats).

Exptal stage	Pool	Lawn	Hummock
All	U > C	U > C	U > C
I	U > C	U > C	U > C
II	U = C	U > C	U > C
III	U > C	U = C	U = C

Significant results (i.e. $p<0.05$) shown by >
Non-significant comparisons shown by =

between uncut and cut cores, and the difference varied between microhabitats in a complex way, presumably due to wetness and vegetation type. Partly as a result of this, the relative fluxes from each of the microhabitats at different times of the year were complicated; at the warmest times (stage II) CH_4-C efflux from uncut cores was greater than that from cut cores for hummocks and lawns, but there was no difference in pools. The same was true, but to a lesser extent, at the coolest times (stage I). Results were mixed from periods of intermediate temperature (stage III).

Half the sampling areas at each site at MH and CR had all their green matter removed in September 1982, in such a way that there remained an equal representation of microhabitat types for uncut and cut areas. The initial biomass removed is shown in Table 4.27. On subsequent field visits any new growth in the cut sampling areas was removed prior to putting out the surface samplers. The dry weight of these subsequent samples was usually in the order of 10^{-2} g, although in the warmest months it tended to be an order of magnitude higher.

TABLE 4.27 Initial biomass removed from within field buckets. Dry weight of green matter removed initially from each cut field sampling area; September 1982.

Moor House

Site	Bucket label	Micro-habitat	Dry weight green matter (g)
4-6	72	Pool	1.9
	71	Lawn	31.5
	45	Hummock	39.0
7-9	78	Pool	2.7
	77	Lawn	22.1
	75	Hummock	51.3
10-12	85	Pool	2.6
	83	Lawn	22.8
	81	Hummock	97.1

Mean weights removed (g)

Site	Mean	Micro-habitat	Mean	MH Mean
4-6	24.1	Pool	2.4	30.1
7-9	25.4	Lawn	25.5	
10-12	40.8	Hummock	62.5	

Coom Rigg

Site	Bucket label	Micro-habitat	Dry weight green matter (g)
13	58	Dry	39.5
13	82	Dry	44.0
14	62	Wet	45.9
14	60	Dry	86.4
15	54	Wet	42.9
15	56	Dry	68.5
16	47	Wet	46.6
16	68	Dry	48.9
17	49	Wet	39.3
17	51	Wet	81.5

Mean weights removed (g)

Site	Mean	CR Mean
13	41.8	54.4
14	66.2	
15	55.7	
16	47.3	
17	60.4	

and three samples out of a total of 257 yielded more than 1 g of material.

At MH there was no correspondence between the overall wetness of a site and the dry weight of green matter it supported, as quantified by the initial biomass removed. The wettest (site 7-9) and driest

(site 4-6) sites yielded very similar mean weights of material per sampling area of 804 cm^2: 25.4 g and 24.1 g. This compared with the intermediate (in terms of wetness) site 10-12 which yielded 40.8 g. However, the different microhabitats at each site differed markedly in the biomass removed, with pools giving a mean of 2.4 g of material per bucket, lawns 25.5 g and hummocks 62.5 g. The pattern was consistent at each of the three MH sites.

Similarly, at CR there was no consistent rank order of sites in terms of both mean water level and weight of green matter removed, but at each site the 'wet' areas yielded a lower biomass than the 'dry'.

The mean biomass removed from nine buckets at MH was 30.1 g dry weight (MH mean water level -2.6 cm), compared with a mean of 54.4 g dry weight from ten buckets at CR (CR mean water level -1.7 cm).

FIG. 4.30 Seasonal methane flux from uncut and cut areas, Moor House and Coom Rigg, 1982-1983

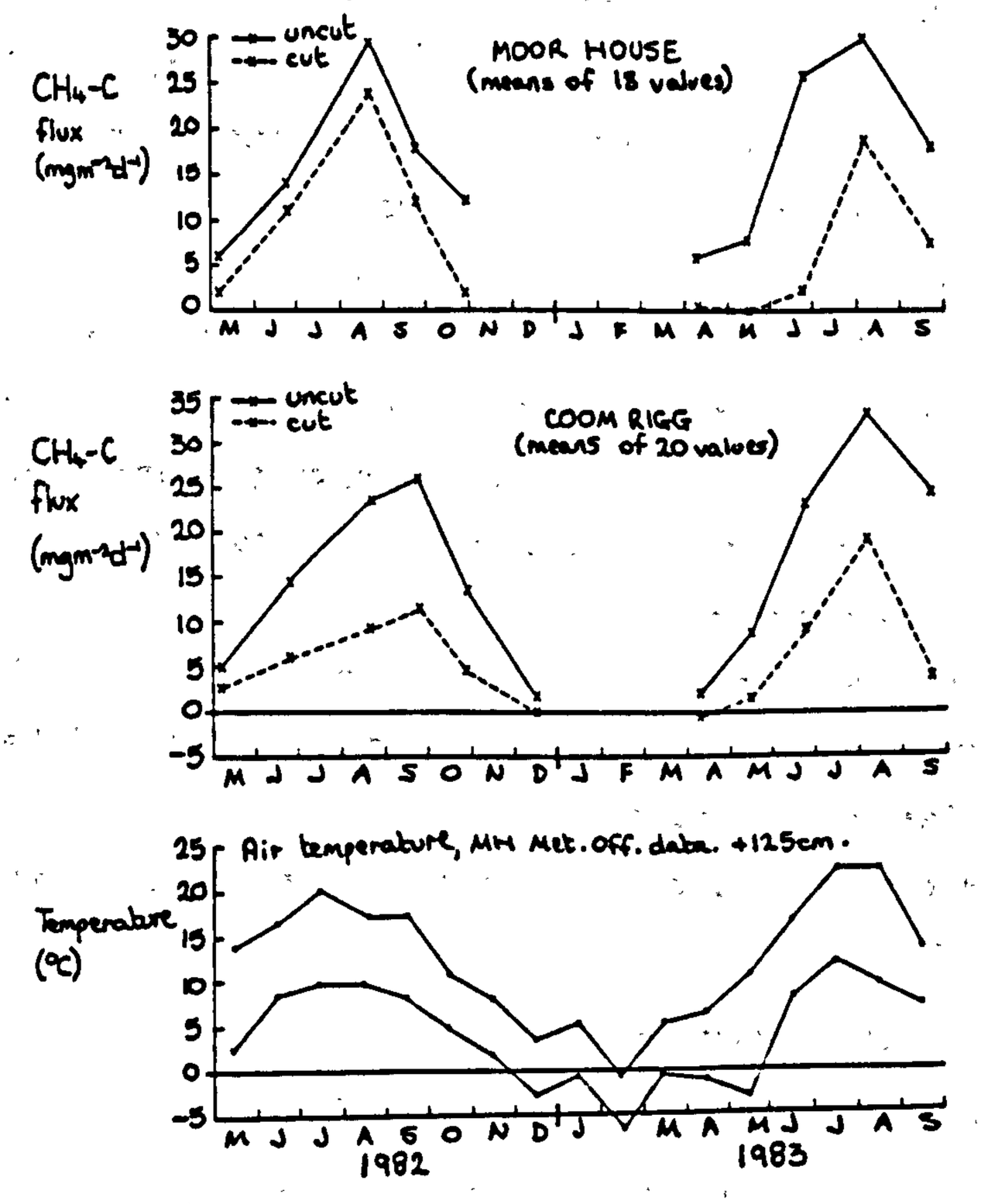


Fig. 4.30 illustrates the seasonal change in methane flux from uncut and cut sampling areas at MH and CR. The monthly mean (Met. Off.) maximum and minimum air temperatures are also shown. The gas flux plots show the mean of all samples taken at each of the two sites on all field visits between May 1982 and September 1983.

As in the garden, removal of the green matter significantly ($p<0.001$, Table 4.15) reduced the efflux of methane and the effect was consistent on all field visits at both sites. At MH the difference in flux was 8.4 mg m^{-2} d^{-1} CH_4-C (uncut mean 16.8 mg m^{-2} d^{-1}, cut mean 8.4 mg m^{-2} d^{-1}) representing a 50% drop in mass of CH_4-C from MH over the study period. At CR the difference was even greater, the uncut mean flux was 17.0 mg m^{-2} d^{-1} compared with 6.3 mg m^{-2} d^{-1} from cut areas, i.e. a drop of about 63%. These figures represent a drop of 0.28 mg m^{-2} d^{-1} CH_4-C g^{-1} dry weight of initial biomass removed at MH and a corresponding fall of 0.20 mg m^{-2} d^{-1} g^{-1} dry weight at CR. The corresponding figures for the garden core microhabitats range over and order of magnitude either side of the field values: a drop of 3 mg m^{-2} d^{-1} CH_4-C g^{-1} dry weight of initial biomass removed from the garden pools; and 0.03 mg m^{-2} d^{-1} for lawns and hummocks.

As in the garden cores, the general seasonal trends in methane flux were similar in uncut and cut sampling areas, the minima and maxima coinciding at each site, but there was variation in the absolute difference between the two fluxes at different times of the year. At MH this seasonal effect was not significant (TIME.CUT interaction, Table 4.15) but at CR it was highly significant ($p<0.001$, Table 4.16), the biggest differences between uncut and cut area fluxes occurring around the peak in flux.

There was some evidence for a slower pick-up and a faster fall-off of flux above areas from which the green matter had been removed. This was particularly noticeable at the end of 1982 and the beginning of 1983 at MH, and at the onset of both 1982 and 1983 seasons and the end of the 1983 at CR (Fig 4.30).

b) Effect of the water level

The relative importance of the microhabitats for CH_4-C flux was little affected by the removal of the green matter (Table 4.14), although, as already discussed, absolute fluxes differed. The main

difference was in the relative importance of pools and lawns; although there was little change in the absolute methane flux from lawns when the green matter was removed (UL=18 mg m^{-2} d^{-1}, CL=17 mg m^{-2} d^{-1}), there was a larger fall in pool flux (UP=49 mg m^{-2} d^{-1}; CP=34 mg m^{-2} d^{-1}). Hence, in cut control cores there was no significant difference between CP and CL over the year, compared to a significantly higher flux from UP than from UL controls.

It is convenient to describe here the comparative effects on some uncut and cut experimental cores representing different microhabitats which were subjected to similar water level changes. This contrasts with the foregoing account which compared uncut and cut control cores, in which water levels remained constant. Comparing the effect of lowering the water level by -5 cm I→II in uncut and cut experimental lawn cores with the corresponding experimental hummock cores (CH2 & CH4 and UH5 & UH7) it can be seen that (Table 4.28) both microhabitat cut core groups showed a similar stage II CH_4-C flux of 32 mg m^{-2} d^{-1} (CH) and 35 mg m^{-2} d^{-1} (CL), whereas the mean stage II flux from the

TABLE 4.28 Summary of mean methane (CH_4-C) fluxes from uncut and cut experimental cores (mg m^{-2} d^{-1}).

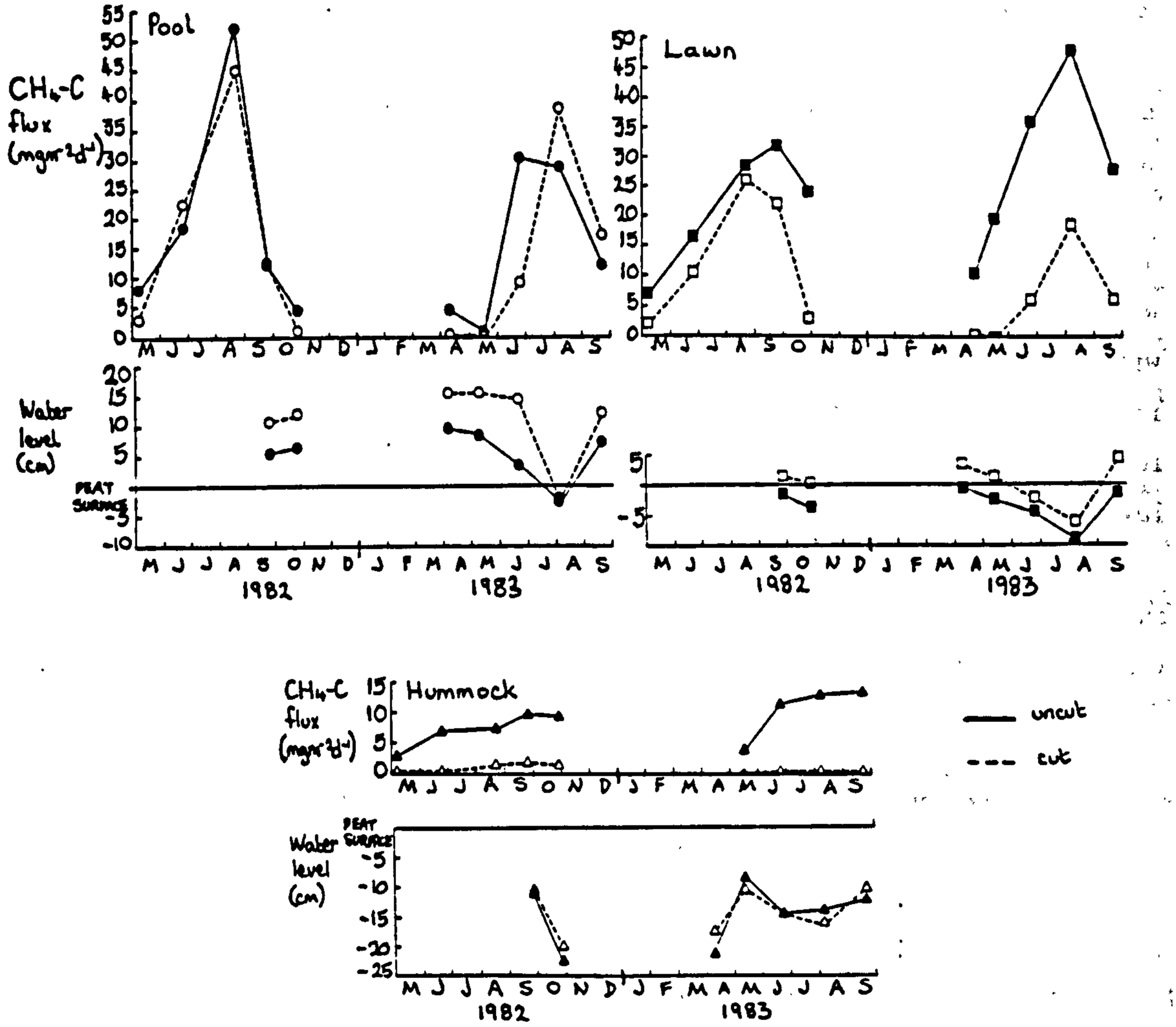
	Pool		Lawn		Hummock			
					Experimental groups			
					H5,H7	H10,H11	H2,H4	H6,H9
Exp^{tal} stage	Uncut	Cut	Uncut	Cut	Uncut		Cut	
All*	74	30	30	16	32	27	43	61
I	9	4	4	6	9		12	11
II	125	67	35	35	61	51	32	31
III	67	30	18	10	35	27	90	144

* mean of stages I-III

uncut cores was almost twice as fast from the hummocks (61 mg m^{-2} d^{-1}) as from the lawns (35 mg m^{-2} d^{-1}). In both stages the hummock core water levels were about 5 cm lower than those of the lawn cores.

Turning now to the field results, the changes in water level and CH_4-C flux in the uncut and cut sampling areas of each microhabitat at MH are shown in Fig. 4.31. Table 4.29 shows the mean methane efflux

FIG. 4.31 Seasonal changes in water level and methane flux from uncut and cut microhabitats, Moor House, 1982-1983. Mean values of 3.



from the uncut and cut sampling areas and illustrates the differences *between microhabitats* at MH over the study period.

It is clear from Fig. 4.31 that removal of the green matter affects the methane efflux from the three microhabitats to varying degrees. In all microhabitats the mean methane efflux dropped when the green matter was removed, though the difference was inconsistent and insignificant over pool areas, where the mean CH_4-C flux dropped from 17.1 mg m^{-2} d^{-1} to 14.9 mg m^{-2} d^{-1}. This represents a reduction of 13%, or 0.9 mg m^{-2} d^{-1} g^{-1} dry weight of green matter removed. There was a bigger effect on efflux from lawns, which fell from

25.1 mg m^{-2} d^{-1} to 9.5 mg m^{-2} d^{-1} (62%) or 0.6 mg m^{-2} d^{-1} g^{-1} dry weight removed. The mean efflux of methane from hummocks dropped by 7.6 to 0.6 mg m^{-2} d^{-1} (93%), which represents 0.1 mg m^{-2} d^{-1} g^{-1} dry weight of material removed.

TABLE 4.29 Summary statistics for water level and gas flux from uncut and cut microhabitats at Moor House, 1982-83. Mean values, ±SE, of n data items.

	Microhabitat Pool	n	Lawn	n	Hummock	n
Water level (cm)						
Uncut	+6.0 ±1.0	24	-3.1 ±0.6	24	-15.2 ±1.4	24
Cut	+10.7 ±1.3	24	+0.4 ±0.7	24	-14.1 ±1.2	24
CH_4-C efflux (mg m^{-2} d^{-1})						
Uncut	17.1 ±3.8	30	25.1 ±5.3	30	9.2 ±1.3	30
Cut	14.9 ±3.8	30	9.5 ±2.7	30	0.6 ±0.2	30
CO_2-C efflux (mg m^{-2} d^{-1})						
Uncut	59 ±14	30	80 ±18	30	390 ±39	30
Cut	84 ±16	29	61 ±17	30	314 ±49	30

Hence, lawns showed the largest absolute reduction in methane efflux, but in relative terms there was an increase in the proportional reduction of methane flux from wetter to drier microhabitats and a concurrent decrease in the rate of flux reduction per unit weight of green matter removed.

The mean fluxes for methane from the garden uncut and cut experimental cores for each stage of the experiment, and the annual mean flux, are given in Table 4.28 (cf Table 4.25 for uncut and cut control cores). Where uncut and cut experimental cores *within microhabitat* types had insignificantly different water levels (see Table 4.3) they were tested for differences in flux using the Wilcoxon matched-pairs test. In practice, this allowed comparison between uncut and cut lawn cores at every stage of the experiment, and between uncut and cut hummock cores in stages I (all cores), II (cores with water levels

nominally at -10 cm). In addition, as for the uncut cores (Fig. 4.24), differences in gas flux between successive stages of the garden experiment were tested for significance in control and experimental cores. The results are summarised in Table 4.30. Fig. 4.32 shows the flux of methane from cut control and experimental cores (cf Fig. 4.23 for uncut core fluxes).

TABLE 4.30 Summary of statistically significant changes in gas flux from cut garden cores, December 1982 to December 1983.

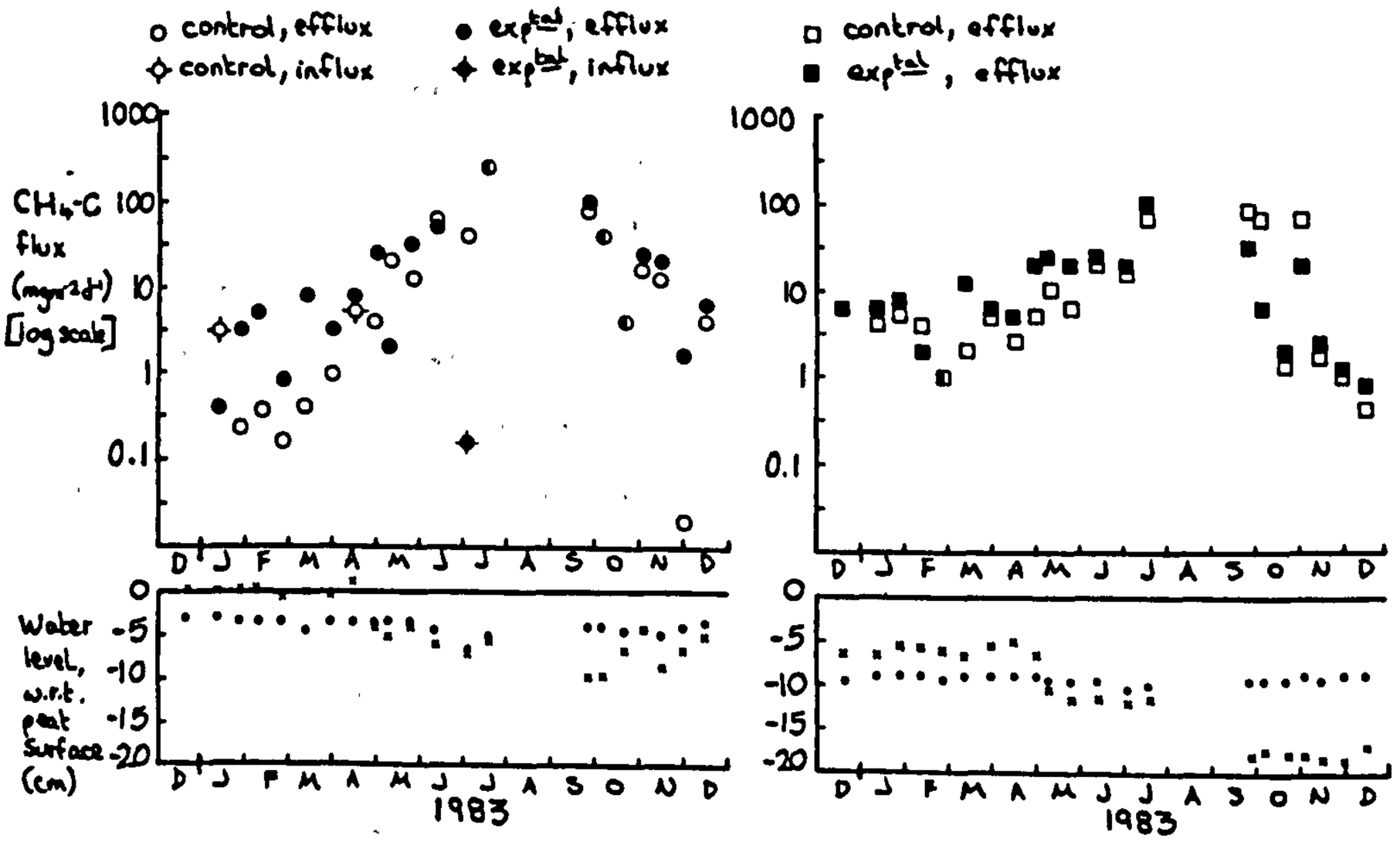
	Cut pool		Cut lawn		Cut hummock		
	Control	Exp^{tal}	Control	Exp^{tal}	Control	Exp^{tal} H2, H4	Exp^{tal} H5, H9
CH_4	-	-	I<II	I<II	-	I<II	-
CO_2	I<II	I<II	I<II>III	I<II	I<II<III	I<II>III	I<II

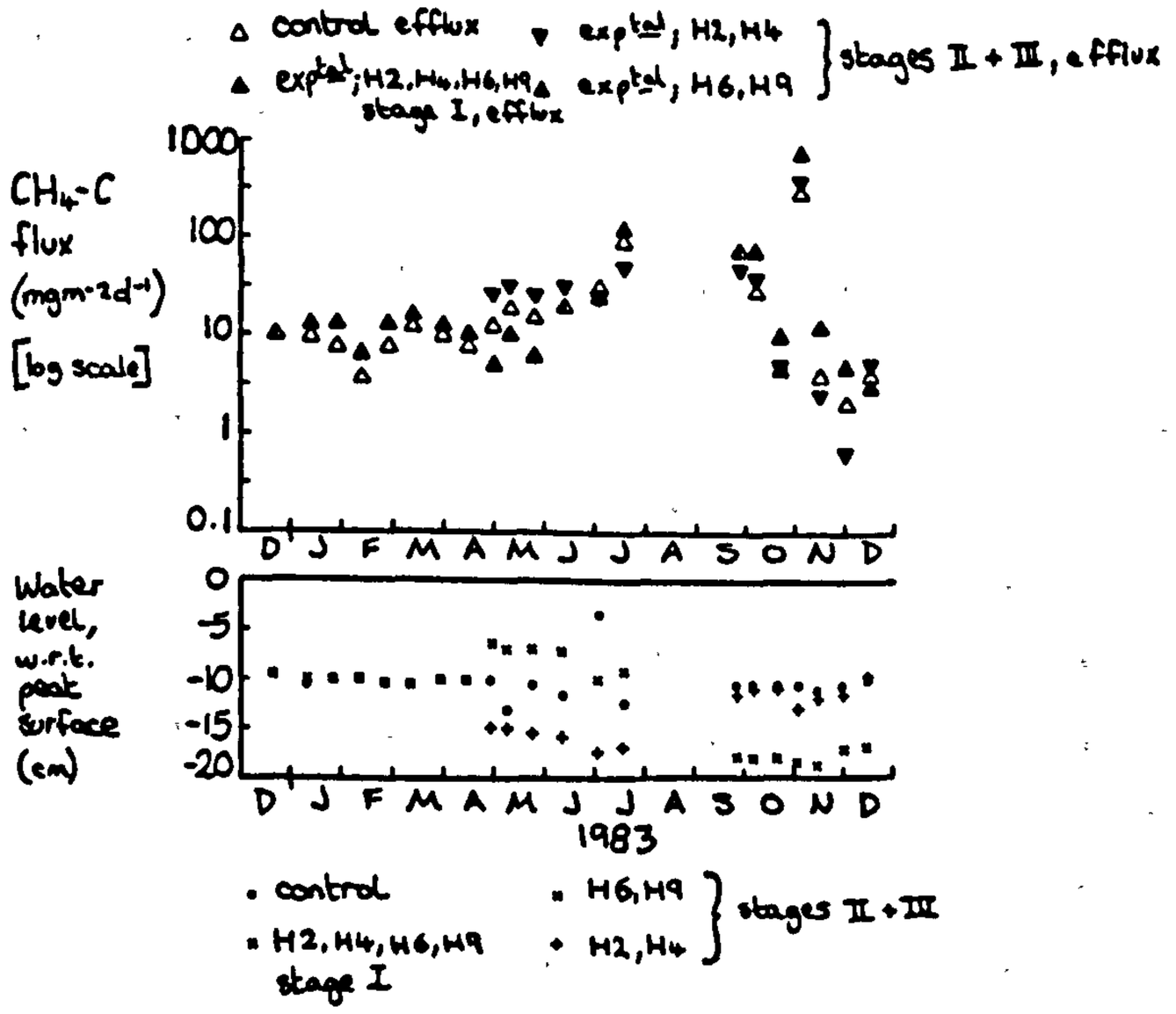
Stage I Dec 1982-Apr 1983
II Apr 1983-Jul 1983
III Sep 1983-Dec 1983

The mean annual CH_4-C flux was 30 mg m^{-2} d^{-1} from the uncut experimental lawns, and only 16 mg m^{-2} d^{-1} from the cut cores. Stage by stage, the most significant difference between cut and uncut cores occurred at the coldest times of the year. In stage I the uncut experimental lawn flux was 4 mg m^{-2} d^{-1} compared with 6 mg m^{-2} d^{-1} from the cut lawns ($p<0.05$). During stage II both groups gave a mean flux of 35 mg m^{-2} d^{-1}. This increase was simultaneous with a drop of approximately 5 cm in the water levels. A further drop of about 8 cm in the water levels for stage III corresponded with a drop in methane flux. These results suggest an overriding temperature effect. A larger decrease occurred over the cut cores compared with the uncut, though the mean fluxes for stage III were insignificantly different (UL 18 mg m^{-2} d^{-1}, CL 10 mg m^{-2} d^{-1}).

During stage I the uncut and cut hummock experimental core water levels were about 10 cm below the peat surface and the fluxes from the cores were insignificantly different (CH flux 12 mg m^{-2} d^{-1}, UH flux 9 mg m^{-2} d^{-1}). Water levels were lowered to approximately -16.5 cm for stage II (cores CH2 & CH4 and UH5 & UH7). Corresponding fluxes were 32 mg m^{-2} d^{-1} from the cut hummocks and 61 mg m^{-2} d^{-1} from the

FIG. 4.32 Surface methane flux from cut control and experimental garden peat cores, December 1982 - December 1983





uncut cores; an increase of about twice as much from uncut cores compared with cut, for the same drop in water level. The difference

in flux from the uncut and cut cores was significant at the 5% level, and this contrasts with the non-significant difference in stage II fluxes from CL and UL cores.

A direct comparison for stage III could only be made between CH2 & CH4 and UH10 & UH11, both groups having a mean water level of about -11.5 cm. The mean fluxes were 90 mg m^{-2} d^{-1} (CH) and 27 mg m^{-2} d^{-1} (UH), a reversal of the pattern seen in stage II where the uncut cores gave the highest flux (51 mg m^{-2} d^{-1} cf 32 mg m^{-2} d^{-1} from CR). Thus methane flux from the cut hummock group increased roughly three-fold, whereas that from the uncut group halved, approximately. The explanation may appear to lie in the water levels which were increased (made shallower) by +5 cm in cores CH2 & CH4 for stage III from stage II, whilst those of UH10 & UH11 were simultaneously lowered (made deeper) by -5 cm. However, an increase of +10 cm in the water level in the uncut cores UH5 & UH7 did not correspond to an increase in methane flux. In fact, both groups of cut experimental cores showed an increase in flux from II to III, despite opposite changes in their water levels, and both groups of uncut hummock cores showed a decrease in flux II→III, also despite opposite trends in their water levels.

Thus, it is clear from the experimental core results, as from those of the controls, that removing the surface vegetation can significantly affect the methane flux, resulting in reduced annual mean fluxes. However, any differential response to changes in water level resulting from removal of the vegetation is not clear. Since water level has been shown to be a secondary influential factor *within* microhabitats, this is perhaps to be expected. The effect on flux of removing the green matter is probably partly (if not entirely) mediated through temperature effects, and since these are complicated by differences in average temperature, rate of change of temperature, and vegetation type, it is unlikely that any, less major, responses to water level changes would become clear. In the field, the differences in flux between the uncut and cut areas were somewhat larger, on average, in 1983 than 1982, which further supports the notion of a temperature effect.

Although there were differences in the mean response of CH_4-C flux to cutting at the three MH sites (Table 4.31), none of the inter-

site differences were apparently significant according to the results of three analyses of variance (CUT.SITE interactions, Table 4.15). In contrast to this, the mean response of CH_4-C flux at the five CR sites was significantly different (Table 4.16). The mean dry weight of material removed from each cut bucket at the CR sites was 41.8 g, 66.2 g, 55.7 g, 47.8 g and 60.4 g for sites 13-17, respectively.

TABLE 4.31 Summary statistics for water level and gas flux of uncut and cut areas at Moor House. Mean values, ±SE, of n data items.

	Site 4-6	n	Site 7-9	n	Site 10-12	n
Water level (cm)						
Uncut	-6.5 ±2.1	24	-1.5 ±2.0	24	-4.3 ±2.2	24
Cut	-2.7 ±2.6	24	+0.1 ±2.5	24	-0.5 ±1.2	24
CH_4-C efflux (mg m^{-2} d^{-1})						
Uncut	16.9 ±2.0	30	7.8 ±1.8	30	25.5 ±4.1	30
Cut	5.7 ±1.5	30	6.1 ±2.0	30	13.3 ±4.2	30
CO_2-C efflux (mg m^{-2} d^{-1})						
Uncut	213 ±50	30	190 ±44	30	127 ±29	30
Cut	166 ±34	29	166 ±40	30	124 ±27	30

Table 4.32 summarises the results of a series of t-tests to determine the significance of the measured effect on gas flux of the removal of green matter at each of the CR sites. Table 4.13 gives the mean values tested. At all sites except 17 the CH_4-C efflux was reduced significantly ($p<0.01$) by the removal of the green matter.

TABLE 4.32 Significance of response of gas flux to removal of green matter at Coom Rigg sites.

Site	CH_4	CO_2
13	***	NS
14	***	NS
15	**	*
16	***	*
17	NS	*

The mean reduction varied from 1.9 mg m^{-2} d^{-1} at site 17 (15%) to 14.2 mg m^{-2} d^{-1} at site 13 (65%). Of the four sites at which a significant response was recorded, the proportional reduction in flux on cutting increased with increasing dryness of the site. A similar result was seen for the progression from pools to hummocks at MH. However, in contrast to the MH result, there was no concurrent decrease in the rate of flux reduction per gram dry weight of green matter removed. For the four significant sites, the value was remarkably constant at between 0.2 and 0.3 mg m^{-2} d^{-1} g^{-1} drop. The proportional reduction in methane flux did not correspond in rank order to the absolute 'increase' in water level which resulted directly from cutting.

It would appear from these results that the variation in the extent of the reduction in methane efflux is associated not directly with water level or the mass of material removed, but with some other site characteristic; perhaps partly with the sort of vegetation removed.

c) Relative importance of temperature and water level

Data collected from all cut garden cores were subjected to (linear) individual variable and multiple regression analyses, as described for the intact cores in Section 4.2.4, Methane Flux (relative importance of temperature and water level), which should be consulted for details of procedure. The dependent variable was CH_4-C flux (mg m^{-2} d^{-1}) and the independent variables used were the same as those for the uncut core analyses (Table 4.19).

Table 4.33 gives the r^2 values for each pair of individual variables. Appendix Kb shows the individual variable and multiple linear regression equations which gave the highest value of r^2 for each data set analysed. The Tables should be compared with Table 4.20 and Appendix Ka which give the corresponding results for the uncut cores.

Taking all samples together, the importance of temperature effects on methane flux decreased when the cores were cut and the water level became relatively more important, but still had only a small influence (r^2=0.2). The decrease in the effect of the temperature increased with the dryness of the microhabitat: compare r^2=0.64 (UP) and r^2=0.62 (CP), with r^2=0.70-0.80 (UH) and r^2=0.25

(CH). In uncut cores the least important temperature variable was that of the air temperature at the time of sampling, but when the green matter was removed from lawns and pools this apparently became

TABLE 4.33 Summary of results from linear regression analyses of gas flux from cut garden peat cores on temperature and water level. Individual variable coefficients of determination, r^2. Signs indicate those of r, the correlation coefficient. A full description of variables is given in Table 4.19.

	Cut pool		Cut lawn		Cut hummock	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
All records						
x_1 Med. interface 2d temp.	0.61	0.70	0.60	0.64	0.25	0.76
x_6 Air temp. at record (sampling)	0.63	0.59	0.60	0.56	0.20	0.70
x_5 Calculated mean peat temp. since last sampling	0.62	0.70	0.57	0.61	0.11	0.74
x_4 Water level (no growth)	-0.09	-0.34	0.19	-0.26	-0.14	-0.23
⟨10 °C						
x_1 Med. interface 2d temp.	-0.16	0.22	0.19	0.01	-0.00	0.19
x_6 Air temp. at record (sampling)	0.31	-0.21	0.18	-0.10	0.30	0.22
x_5 Calculated mean peat temp. since last sampling	0.19	0.48	0.06	0.17	0.08	0.19
x_4 Water level (no growth)	-0.15	-0.39	0.38	-0.58	0.00	-0.57
⟩10 °C						
x_1 Med. interface 2d temp.	0.60	0.61	0.50	0.52	0.08	0.68
x_6 Air temp. at record (sampling)	0.64	0.41	0.49	0.34	-0.04	0.55
x_5 Calculated mean peat temp. since last sampling	0.62	0.64	0.50	0.53	-0.07	0.71
x_4 Water level (no growth)	-0.04	-0.36	0.25	-0.29	-0.17	-0.23

the most important influence. In hummocks it remained unimportant, that of the peat temperature being more so.

There was a certain amount of variation in the apparent temperature influence on CH_4-C flux from cut cores, and to a lesser extent that of water level, in different seasons. At cooler times of the year, when the air temperature was less than 10°C, the correlation between CH_4-C flux from uncut cores and temperature fell, but increased for that from cut cores, and whereas the peat temperature was most important in uncut cores, air temperature was most important for cut cores.

The results from warmer times of the year are more in agreement between uncut and cut cores, viz. temperature remains closely

correlated with CH_4-C flux, but the importance of the water level increases with dryness of habitat and thus is relatively more important in hummocks than in pools and lawns. Indeed, in cut hummocks it was more important than temperature (in contrast to uncut hummock cores).

The importance of the water level to CH_4-C flux from cut cores at warmer times of year increased with dryness of habitat.

Thus, all records taken together, there is little difference between the results from uncut and cut cores; temperature is the most closely-correlated factor with CH_4-C flux and water level is only of (minor) significance in hummocks where r^2 values may reach about 0.20. On cutting, the importance of temperature was somewhat reduced and water level became relatively more important (but was still only weakly correlated). These effects increased with increasing dryness of the habitat. In uncut cores there was little difference in the r^2 values for the temperature variables, but cut cores varied in this respect; air temperature was apparently the most important temperature variable in cut lawns and cut pools, compared with peat temperature in hummocks.

Correlation analyses were also carried out on field data from cut areas following the same procedure as that for the uncut area data reported above. The data sets and variables tested were the same (see Tables 4.21 and 4.22). The full table of r^2 values for the variables used in the analysis without the interface temperatures are given in Appendix Le, which should be compared with Appendix La (uncut areas). The restricted data sets, that is, those including the interface temperatures, showed that these variables were of no significance in their influence on the flux of CH_4-C and since they yielded no other reliable information the corresponding table of r^2 values has not been given. Appendix Lf gives the multiple r^2 values for the regression equations based on data from cut areas. Appendix Lf should be compared with Appendix Lc. In Table 4.34 are reproduced the multiple r^2 values for the full cut data sets, for ease of reference here, and it may be compared with the corresponding Table 4.23 of uncut area results.

TABLE 4.34 Summary of multiple linear regression analyses of gas flux on temperature and water level at Moor House and Coom Rigg. Cut area data only. Variables and units are listed in Table 4.21. Coefficients of determination for linear regressions, and significance of regressions.

	Variables											Data set (full)																	
												CP		CL		CH		MH		site 13		site 14		site 15		site 16		site 17		CR		MH&CR	
	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.
CH_4											+	0.36	**	0.03	ns	0.03	ns	0.03	ns	0.16	ns	0.00	ns	0.32	*	0.00	ns	0.18	ns	0.03	ns	0.00	ns
	+	+	+	+			+	+			+	0.72	**	0.55	ns	0.55	ns	0.37	***	0.68	ns	0.62	ns	0.89	**	0.53	ns	0.62	ns	0.37	***	0.35	***
	+	+	+	+					+	+	+	0.72	**	0.55	ns	0.55	ns	0.37	***	0.67	ns	0.62	ns	0.89	**	0.37	ns	0.62	ns	0.36	***	0.35	***
CO_2											+	0.68	***	0.54	***	0.03	ns	0.43	***	0.09	ns	0.32	*	0.18	ns	0.48	**	0.30	*	0.27	***	0.31	***
	+	+	+	+			+	+			+	0.94	***	0.73	**	0.87	***	0.65	***	0.94	***	0.92	**	0.97	***	0.77	ns	0.97	***	0.69	***	0.61	***
	+	+	+	+					+	+	+	0.94	***	0.73	**	0.87	***	0.65	***	0.94	***	0.87	*	0.97	***	0.77	ns	0.96	***	0.69	***	0.61	***

It is difficult to provide accurate generalisations of the effect of removing the green matter on the relative influences of water level and the different temperature variables, since there was inconsistency between the results from different sites and microhabitats for each gas. Overall, the effect of temperature became more important, but beyond this the apparent inconsistencies in the results necessitate more detailed descriptions.

Comparing the results from the seven-variable regression analysis (see Section 4.2.4, Methane Efflux - Relative importance of temperature and water level) it is clear that the effect of removing the green matter was not consistent between sites. In some cases the r^2 values and significance levels increased, while in others they fell, between uncut and cut area results.

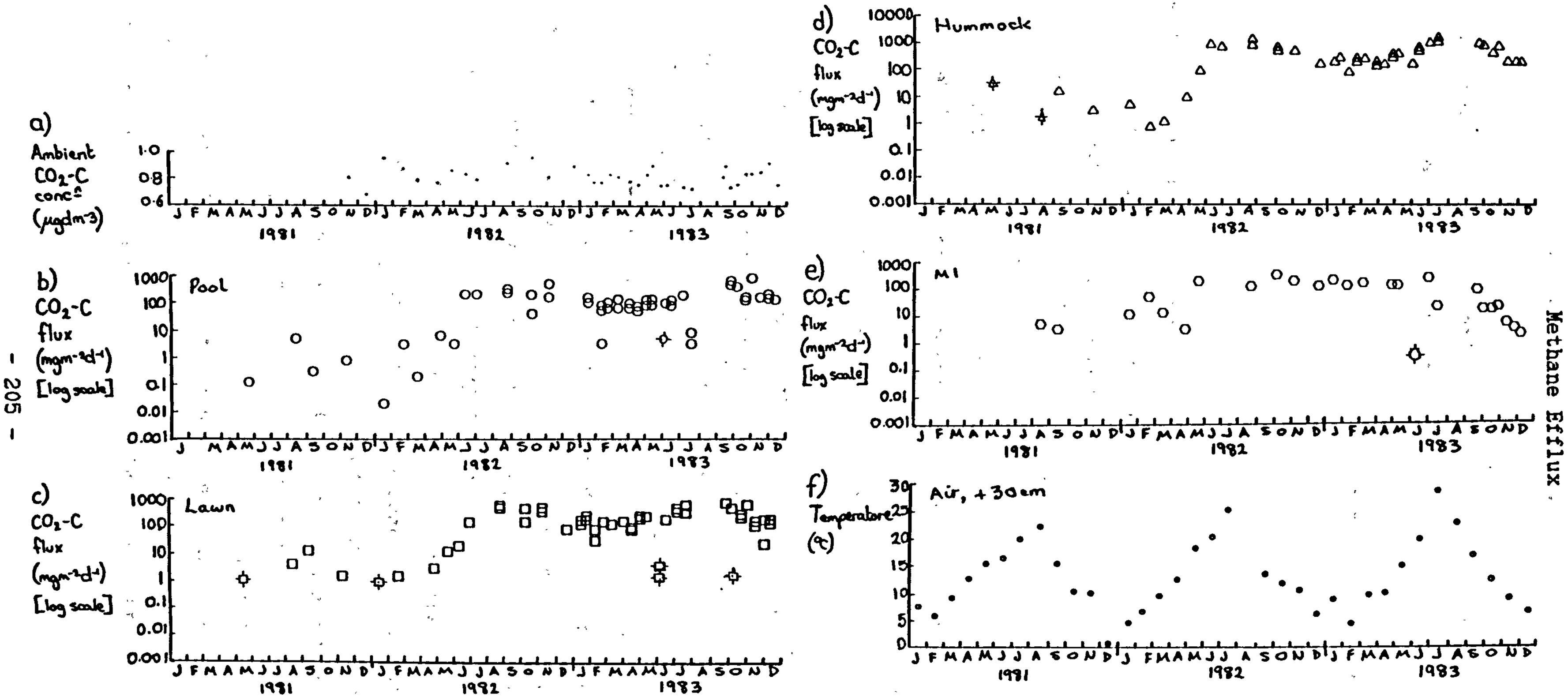
The difference between the seven-variable regression r^2 value which was seen between MH and CR uncut data was not evident when cut area data were used, suggesting that the peat system itself is not responsible for the difference, but that it should be attributed to the quality or quantity of surface vegetation, or both.

As was seen for uncut data, temperature was more important an influence the wetter the habitat, r^2 increasing. When the green matter was removed the relationships between the three microhabitats changed, and each showed quite distinct ranges of r^2 values; temperature and water level accounted for 30-55% and 36%, respectively, of methane efflux variation above pools; temperature for 25-30% and water level none of the variation above lawns, and neither temperature or water level was important for cut hummocks.

Overall, at MH on removal of the green matter, the influence of the temperature on methane efflux became more apparent, whilst the importance of the water level remained unchanged, and low ($r^2<0.03$).

At CR, at the wettest sites (13 and 15), the influence of the temperature variables *dropped* when the green matter was removed and the importance of the water level increased. Thus, the effect on the temperature influence was in contrast to that at the pool and lawn sites at MH, although the increase in the importance of the water level was similar. At CR, at the drier site 17, both temperature and

FIG. 4.33 Seasonal changes in garden surface carbon dioxide flux.
Individual uncut core data.



Open symbols indicate efflux
Closed, crossed symbols indicate influx

water level effects increased in cut areas relative to the uncut, and the water level became more important relative to the temperature.

4.2.5 CARBON DIOXIDE EFFLUX

SEASONAL CHANGES

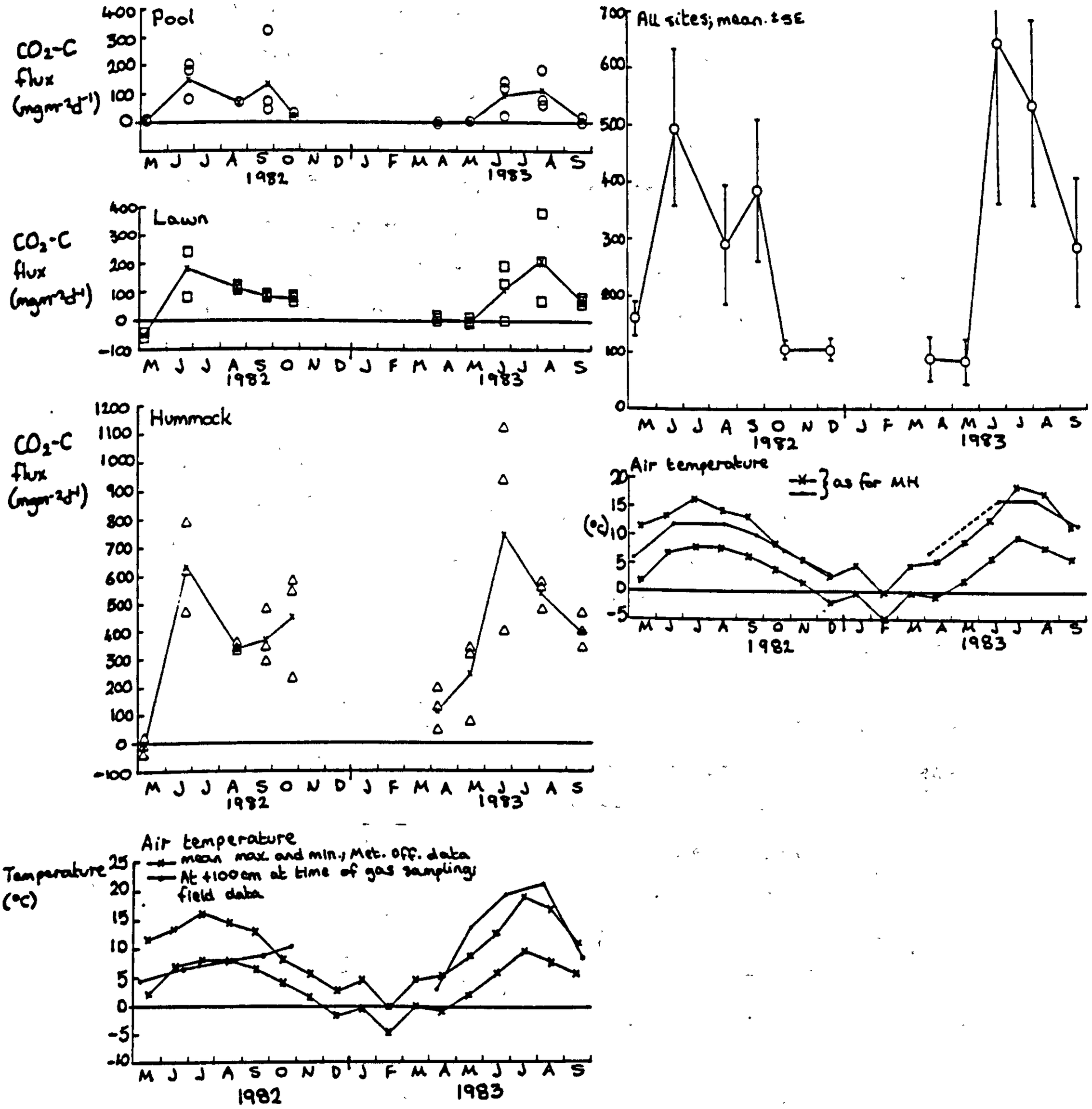
a) Garden

Carbon dioxide flux from each (garden) microhabitat showed a distinct seasonal pattern similar to that revealed for methane (Fig. 4.33). The annual range of flux appears somewhat smaller for carbon dioxide than for methane, giving slightly less marked summer peaks due to the higher absolute flux values and the log scale used in the plot. However, CO_2-C flux picked up in March and April from an annual minimum around 100 mg m^{-2} d^{-1} and peaked between June and September at about 600-650 mg m^{-2} d^{-1}. Thus there was an absolute annual range of 500-550 mg m^{-2} d^{-1}, compared with 100-250 mg m^{-2} d^{-1} CH_4-C in each case, the exact range depending on the microhabitat. In relative terms the CO_2-C flux increased five- to six-fold between the annual minimum and maximum, whereas CH_4-C flux increased roughly one hundred-fold. In general the differences in flux between microhabitats at any time was larger (absolutely) for CO_2-C than for CH_4-C. The annual (1983 data) mean CO_2-C flux for pool, lawn and hummock cores, omitting any negative fluxes, was 196 mg m^{-2} d^{-1}, 235 mg m^{-2} d^{-1} and 512 mg m^{-2} d^{-1}, respectively, and 92 mg m^{-2} d^{-1} for M1, a change of the trend in CH_4-C fluxes which increased in the order lawn, hummock, pool. M1 showed the smallest annual mean figure for both CH_4-C and CO_2-C flux, an effect which was probably attributable to sampling procedure. The difference in the mean annual CO_2-C flux from pool and lawn cores was insignificant, but that of hummocks was significantly different from the other two microhabitats, as judged from the 95% confidence limits of the means. In contrast to CH_4-C flux there appeared to be no switch in the relative importance of the microhabitats at different times of the year in the amount of carbon dioxide they evolve; consistently the hummock flux was greater than that of the pools and lawns, which themselves showed an inconsistent position relative to each other.

Carbon Dioxide Efflux

As for CH_4-C, the flux of CO_2-C corresponded to the general trends in peat and air temperatures but did not reflect short-term temperature changes faithfully (compare Figs. 4.2, 4.9b and 4.33b-e).

FIG. 4.34 Seasonal changes in carbon dioxide flux from uncut sampling areas at Moor House and Coom Rigg. Negative values represent influxes.



Unfortunately, because of the gap in gas flux records mid-July to late September, 1983, it was not possible to determine exactly when the peak CO_2-C or CH_4-C fluxes occurred. Data from 1982 for carbon dioxide suggested a lag, since maximum air and peat temperatures were recorded in late July and the maximum fluxes in late August. Again, as for CH_4-C fluxes, the minimum 1983 carbon dioxide record was for February and coincided with the highest frequency of ice and frost days.

Over the three study years there were nine negative flux results, four of which occurred prior to the use of bucket lids during sampling. Of the remaining five cases, four were on a single sampling day in June 1983 and represented fluxes from one pool, both lawns and the minibog. The final negative flux was recorded for a lawn core in October 1983. Only one such record corresponded in time with a negative methane flux; that of a lawn in May 1981, from the period when foil and polythene were still being used to close the buckets for sampling.

b) Field

Seasonal changes in the rate of CO_2-C loss were highly significant ($p<0.001$) at both MH and CR (Fig. 4.34). Overall, carbon dioxide accounted for about 10x (MH, Table 4.9) and 16x (CR, Table 4.13) the mass of carbon lost as methane.

Above uncut pools, CO_2-C flux increased slowly from about 0-5 mg m^{-2} d^{-1} in May (apparently not before) to its summer peak of between 110 and 150 mg m^{-2} d^{-1} (June to August). The final record of each season, made in October 1982 and September 1983, showed a decline in CO_2-C flux to around 20 mg m^{-2} d^{-1}; that is, the flux had not fallen to its early-season minimum at that time. Thus, despite slightly higher temperatures in 1983 the mean minimum and maximum CO_2-C fluxes were 20 and 40 mg m^{-2} d^{-1} lower than in 1982, respectively. It appears from the pool results at least that the increase in CO_2-C flux begins about a month later than that of CH_4, but then is much more rapid. Ranges of individual site CO_2-C fluxes varied between 0 and 120 mg m^{-2} d^{-1}, with, as for CH_4-C, a tendency for larger variation in the summer months.

Carbon Dioxide Efflux

Overall, lawns accounted for about 25% more CO_2-C loss (mean flux 80 mg m^{-2} d^{-1}) than did pools (mean flux 59 mg m^{-2} d^{-1}). In both years there were negative monthly mean CO_2-C fluxes of up to -50 mg m^{-2} d^{-1} recorded prior to the early summer increase.

The site variation in CO_2-C flux (as for CH_4-C flux) was greater over lawns than over pools, and changed seasonally, although the end of season differences were only 10% as big as the maximum summer differences, whereas the corresponding methane differences persisted to the last field visit of each year.

The mean flux of CO_2-C from hummocks was 390 mg m^{-2} d^{-1}, and thus represented about a 6-fold increase over that of pools and a 5-fold increase over lawns. The rate of increase in the flux, apparently beginning, if slightly more slowly at first, in April rather than May, continued the trend seen between pools and lawns of a faster take-off the drier the microhabitat. The 1982 peak in hummock CO_2-C flux was 620 mg m^{-2} d^{-1}; more than three times that of lawns and about four times that of pools. The 1983 peak was a month earlier than that over pools and lawns, and was 750 mg m^{-2} d^{-1}. In May 1982 the mean carbon dioxide flux was negative, but this did not recur in 1983.

Variation between sites ranged from 40 to 717 mg m^{-2} d^{-1}, and was seasonal, though less obviously so in 1982.

Thus, as for methane, temperature appeared to be correlated with the general seasonal changes in carbon dioxide flux from each of the three microhabitats, and in 1982 all three showed a maximum flux in the month prior to that in which the maximum air temperature was recorded. In 1983 the correspondence was not so consistent; pool and lawn flux maxima occurred a month after that of air temperature, whereas the hummock flux peaked in the month prior to it.

Of the three microhabitats, only hummocks returned a significant ($p<0.01$) correlation coefficient for the relationship between carbon dioxide flux and spot air temperatures; the r^2 value was 0.34. The MH data, all microhabitats clumped together, gave $r^2=0.12$ ($p<0.05$).

At CR the carbon dioxide fluxes were more of the order of the MH hummock fluxes than of either the lawns or pools (Fig. 4.34). The flux reached a maximum of 495 mg m^{-2} d^{-1} in 1982, from 160 mg m^{-2} d^{-1} in May, and 640 mg m^{-2} d^{-1} in 1983, from 85 mg m^{-2} d^{-1} in May. The

summer record standard errors were very large, but again were much reduced early and late in the year. From October to December there was, apparently, no further decline in CO_2-C flux, and the first record of 1983, in April, was insignificantly different from this (about 100 mg m^{-2} d^{-1}). There were no negative carbon dioxide flux records from CR.

The r^2 value for the CR data, clumped, was 0.28 for the correlation between CO_2-C flux and the air temperature measured at the time of the gas record ($p<0.01$, cf $p<0.05$ for MH). Carbon dioxide flux appeared to be more closely related to the (spot) air temperature, in general, than did methane.

The overall mean CO_2-C flux from MH and CR uncut sampling areas was 176 mg m^{-2} d^{-1} (Table 4.9) and 278 mg m^{-2} d^{-1} (Table 4.13), respectively.

As was seen for methane, an analysis of variance carried out on uncut and cut area data together returned a highly significant ($p<0.001$) result for the TIME.SITE interactive effect on CO_2-C flux at CR, but was not significant at MH ($p<0.05$ for CH_4-C at MH).

EFFECT OF THE WATER LEVEL

CO_2-C flux data were treated in the same way as CH_4-C to assess the effect of the water level. The account for methane, above, should be consulted for details of data sets used and analyses carried out. Table 4.3 gives the water levels maintained at each stage of the garden experiment; Figs. 4.35 and 4.36 show the CO_2-C flux (and water levels) for cut control cores and for uncut control and experimental cores, respectively.

a) Between microhabitats - garden

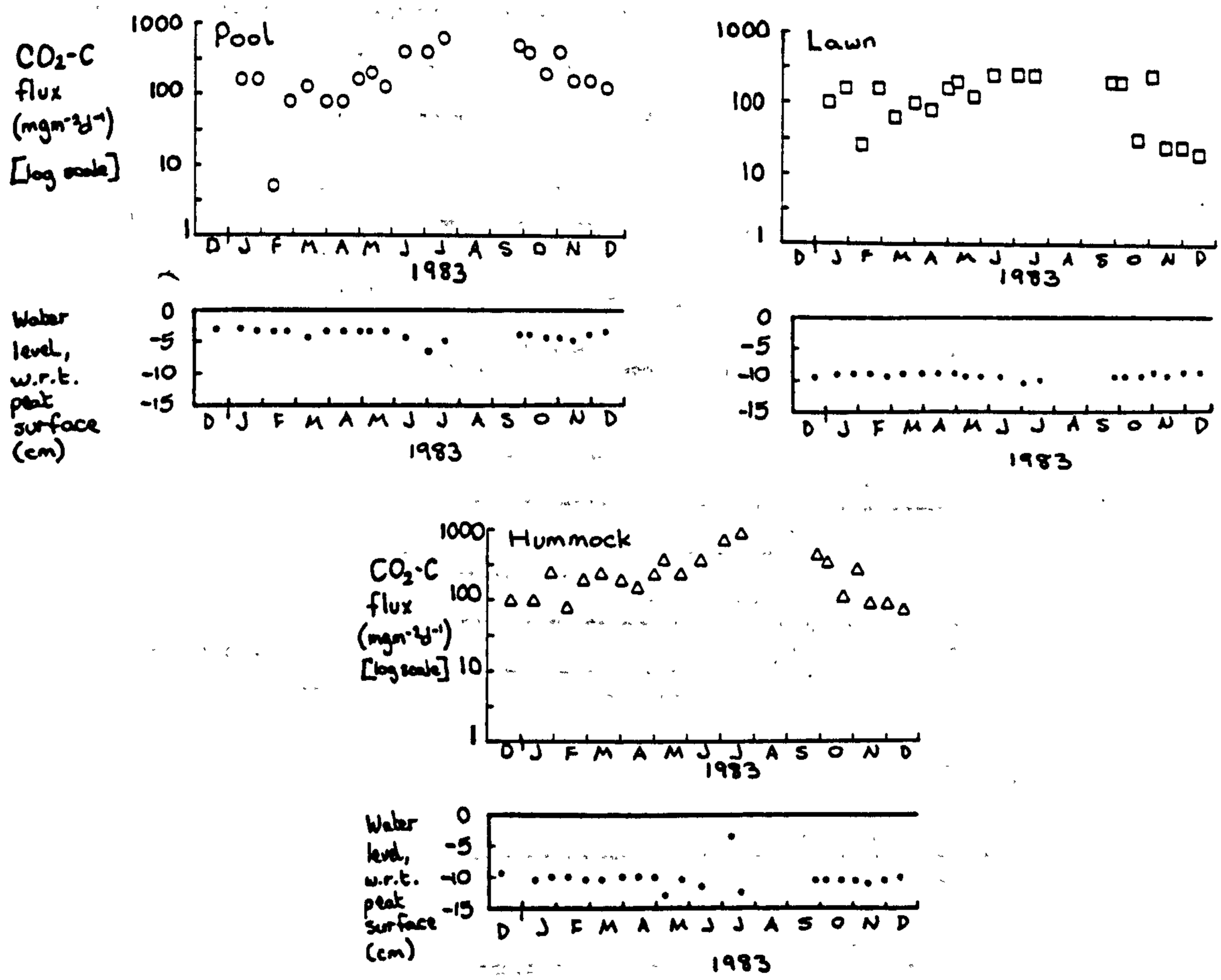
There were significant ($p<0.05$, Table 4.35) differences between the overall mean CO_2-C flux from cut control cores representing the three microhabitats, but the rank order of increase in mean flux did not correspond with that of water level: CO_2-C flux increased in the order lawn (137 mg m^{-2} d^{-1}), pool (232 mg m^{-2} d^{-1}), hummock (291 mg m^{-2} d^{-1}); water levels in the order hummock (-11.0 cm), lawn (-9.2 cm), pool (-4.2 cm, nominal).

TABLE 4.35 Summary of Wilcoxon matched-pairs analyses, comparing uncut and cut control core carbon dioxide fluxes (between microhabitats).

Exp^{tal} stage	Uncut		Cut		
All	L > P	H > L	P > L	H > L	H > P
I	L > P	H > L	P = L	H > L	H > P
II	L > P	H > L	P = L	H > L	H > P
III	†	H > L	P > L	H > L	P > H

Significant results (i.e. $p<0.05$) shown by >
Non-significant comparisons shown by =
† insufficient data

FIG. 4.35 Carbon dioxide flux from garden cut control cores, December 1982 - December 1983



The mean control water levels did not change by more than ±1.6 cm throughout the experimental period in any of the microhabitats, but the fluxes changed significantly, and inconsistently, between microhabitats. These results suggest that, as was seen for CH_4-C flux, the overall annual mean water level may have a rôle in determining the order-of-magnitude of CO_2-C flux from the different microhabitats over the year, but does not appear to be closely associated with smaller or high frequency changes in flux.

b) Within microhabitats - garden

The CO_2-C flux from uncut control and experimental cores and from M1 is shown in Fig. 4.36, and a summary of the results from a series of t-tests to determine whether the mean CO_2-C fluxes from cores in different stages of the experiment were significantly different are shown in Fig. 4.37. A comparison of Fig. 4.37 with Fig. 4.24 shows a close similarity in behaviour between CO_2-C and CH_4-C flux during the garden experiment. Carbon dioxide flux, as that of methane, increased significantly at some stage during the experiment, irrespective of whether water levels were held constant, increased or lowered. Even within the hummock group of cores both an increase and a decrease in

FIG. 4.37 Significant changes in water level and carbon dioxide flux during the garden experiment. A step indicates a significant ($p<0.05$) difference in the mean water level or flux between stages.

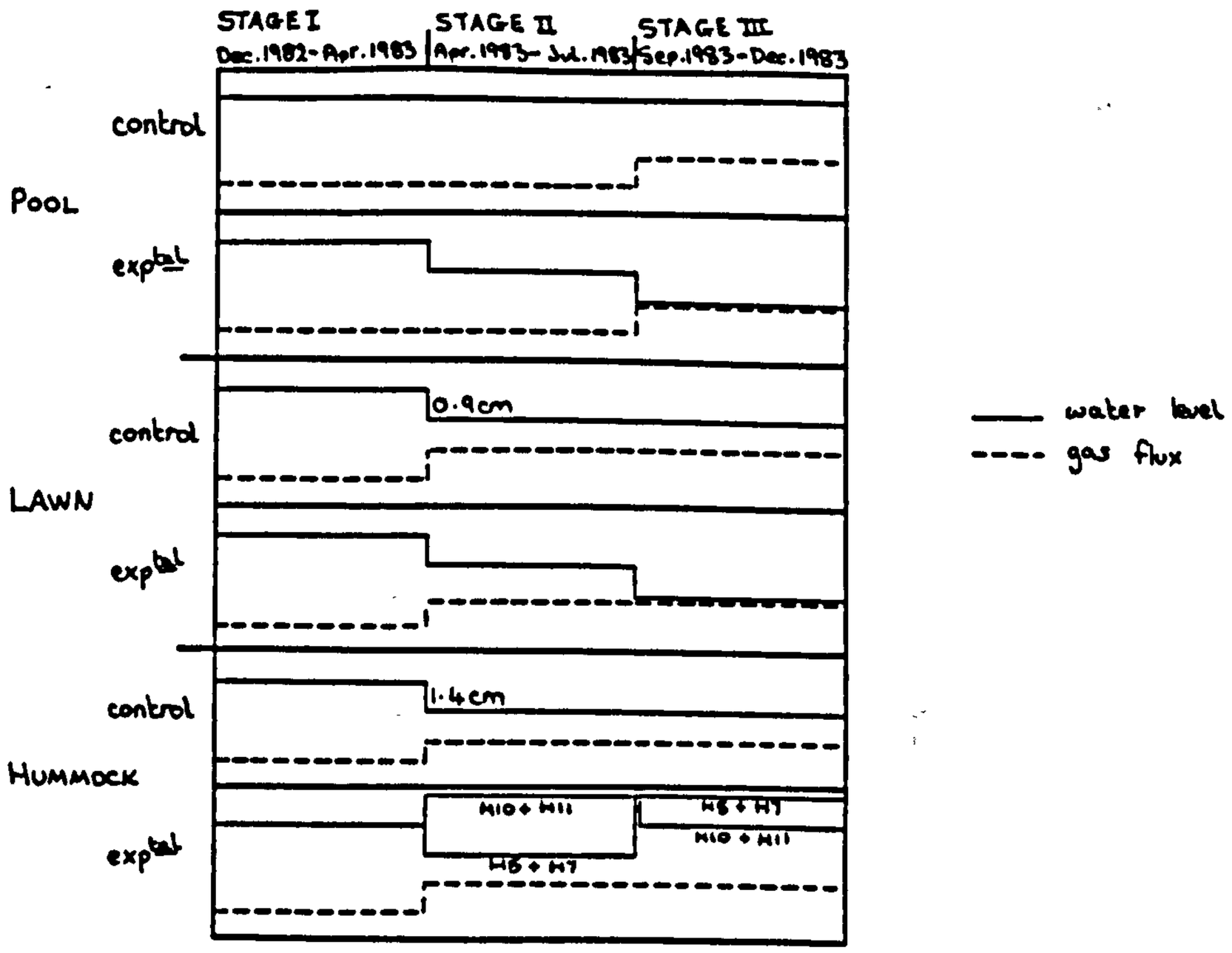
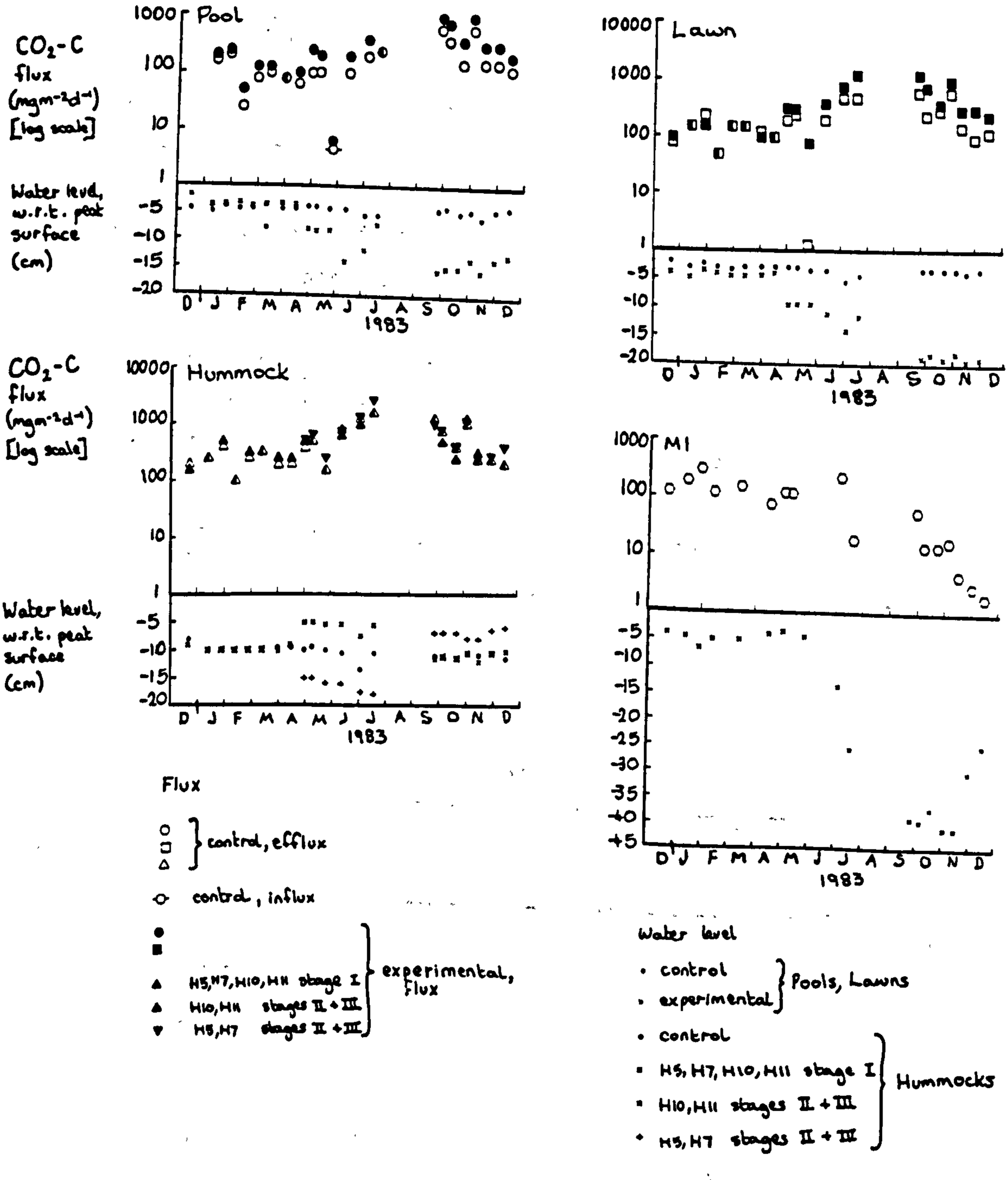


FIG. 4.36 Carbon dioxide flux from garden uncut control and experimental cores, December 1982 - December 1983



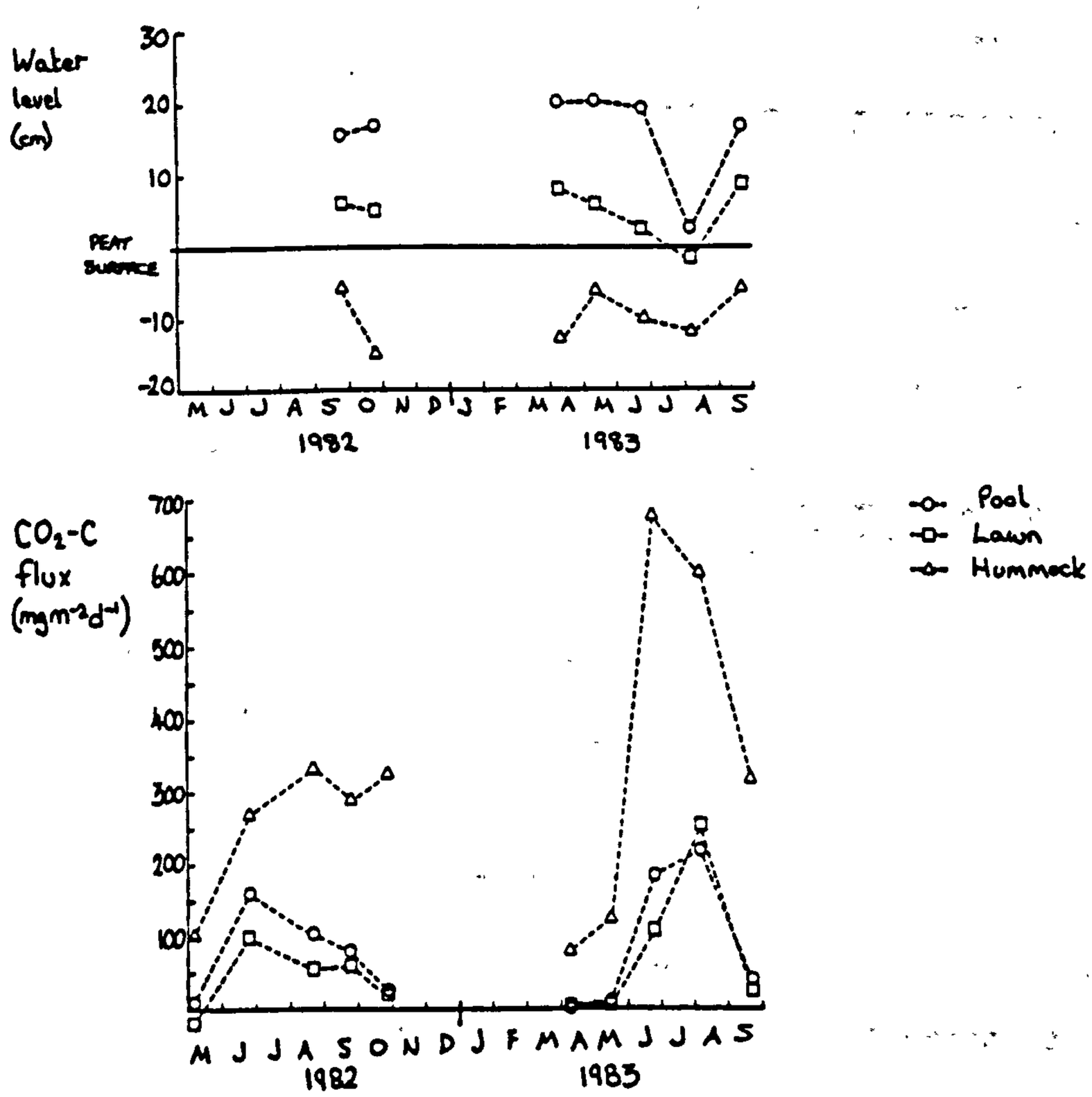
water level of 5 cm (simultaneously in different cores) produced a significant increase in flux. Further, a relatively large increase in

water level of 9.7 cm in H5 & H7 produced no significant flux change. This consistent increase in flux for all microhabitats suggests an overriding temperature effect. It is interesting to note that the main difference between the summary CO_2-C and CH_4-C results is that the increase in CO_2-C flux occurred later than that of CH_4-C (between stages II and III rather than between I and II). This suggests a possible lag in CO_2-C production response (to temperature) in this case. Such a lag between CO_2-C and CH_4-C seasonal take-off was noted from the field results, above.

Fig. 4.37 does not allow any comparison between absolute values for control and experimental cores, and hence obscures some interesting results.

In pools, water level and carbon dioxide flux were significantly different between control and experimental cores at each stage of the experiment; experimental fluxes were higher than those of the controls

FIG. 4.38 Water level and carbon dioxide flux changes (cut sampling areas), Moor House, 1982-1983. Mean values of 3. Negative values indicate an influx.



in every case. The significance levels were $p<0.005$ (I), $p<0.025$ (II) and $p<0.005$ (III). In stages II and III this might be expected because the experimental water levels were lower than those of the controls. These results are in contrast to those for methane, in which there was no significant difference between control and experimental core fluxes. It would appear then that water level has more influence on carbon dioxide than on methane flux, from pools at least. Furthermore, when the differences between control and experimental core fluxes were analysed, they were seen to increase significantly I→II→III, This may in part be due to temperature increases, though air and surface temperatures decreased II→III, but would seem also to be a response to a further drop in water level in the experimental cores relative to the controls, at each stage. As for pools, there was a contrast in results between lawn methane and carbon dioxide fluxes; there was no significant difference between control and experimental lawn methane fluxes as there was for carbon dioxide.

Results from comparing lawn control and experimental cores also suggested that water level had some influence, perhaps after temperature, on CO_2-C flux.

At no stage, for either hummock experimental group, was there a significant difference between the experimental group mean flux and that of the controls, despite significantly different mean water levels.

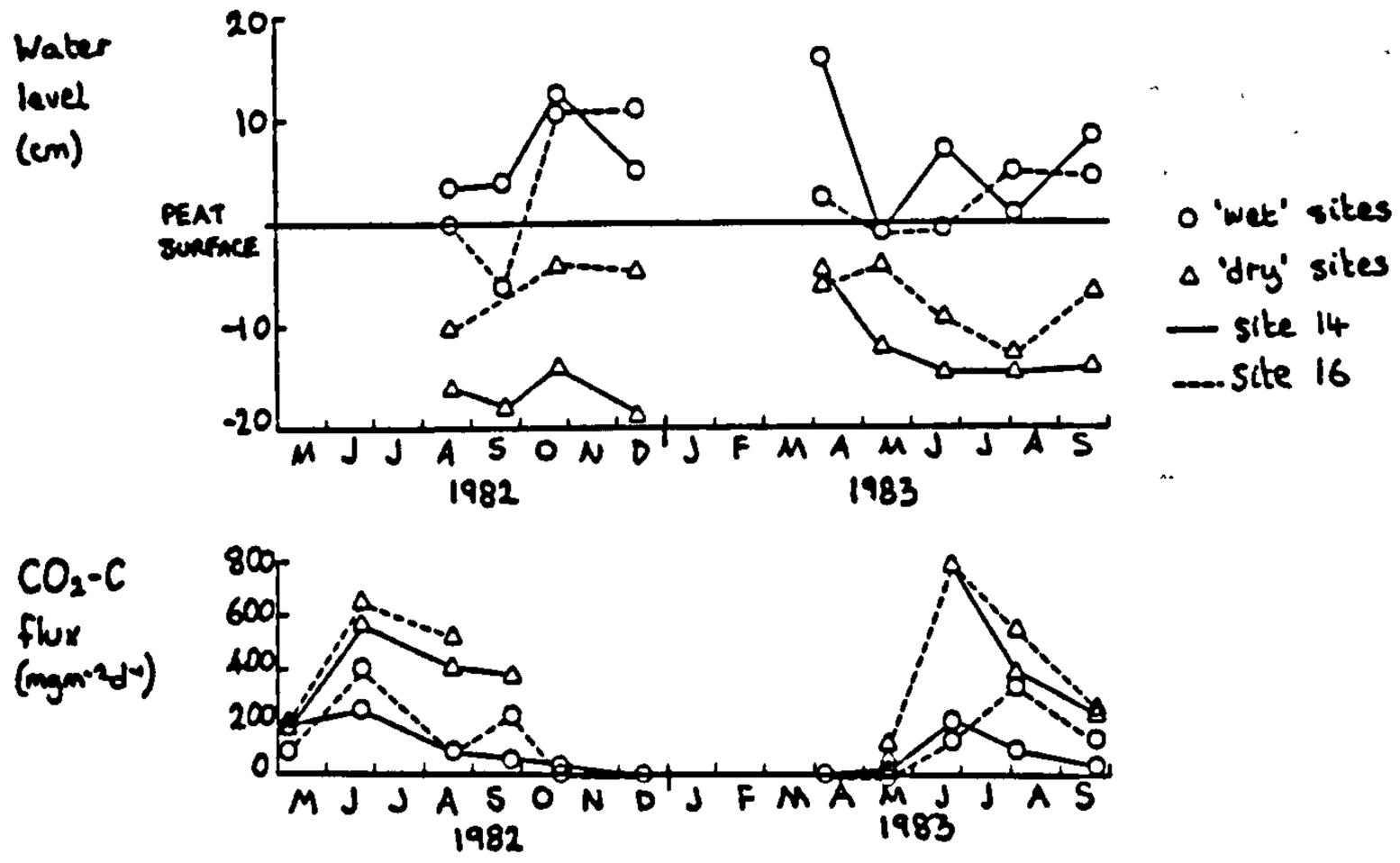
The hummock carbon dioxide flux results thus suggest that water level has no effect on flux from hummocks.

c) Between microhabitats - field

Fig 4.38 shows the changes in water level and CO_2-C flux for cut pools, lawns and hummocks at MH; the corresponding plots for CR wet and dry areas at sites 14 and 16 are given in Fig. 4.39.

At both MH and CR there was a consistent, marked increase in CO_2-C flux on moving from wetter to drier microhabitats ($p<0.001$ for uncut and cut data together). At MH the mean flux was 84 ±16 mg m^{-2} d^{-1}, 61 ±17 mg m^{-2} d^{-1} and 314 ±39 mg m^{-2} d^{-1} CO_2-C for CP, CL and CH, respectively. Cut pools and lawns were fairly similar in

FIG. 4.39 Water level and carbon dioxide flux changes in selected sampling areas, Coom Rigg, 1982-1983



their absolute CO_2-C flux, despite a difference in mean water level of 10.3 cm, but hummock CO_2-C flux was very much higher, although the CH mean water level was only 3.4 cm below that of the CLs.

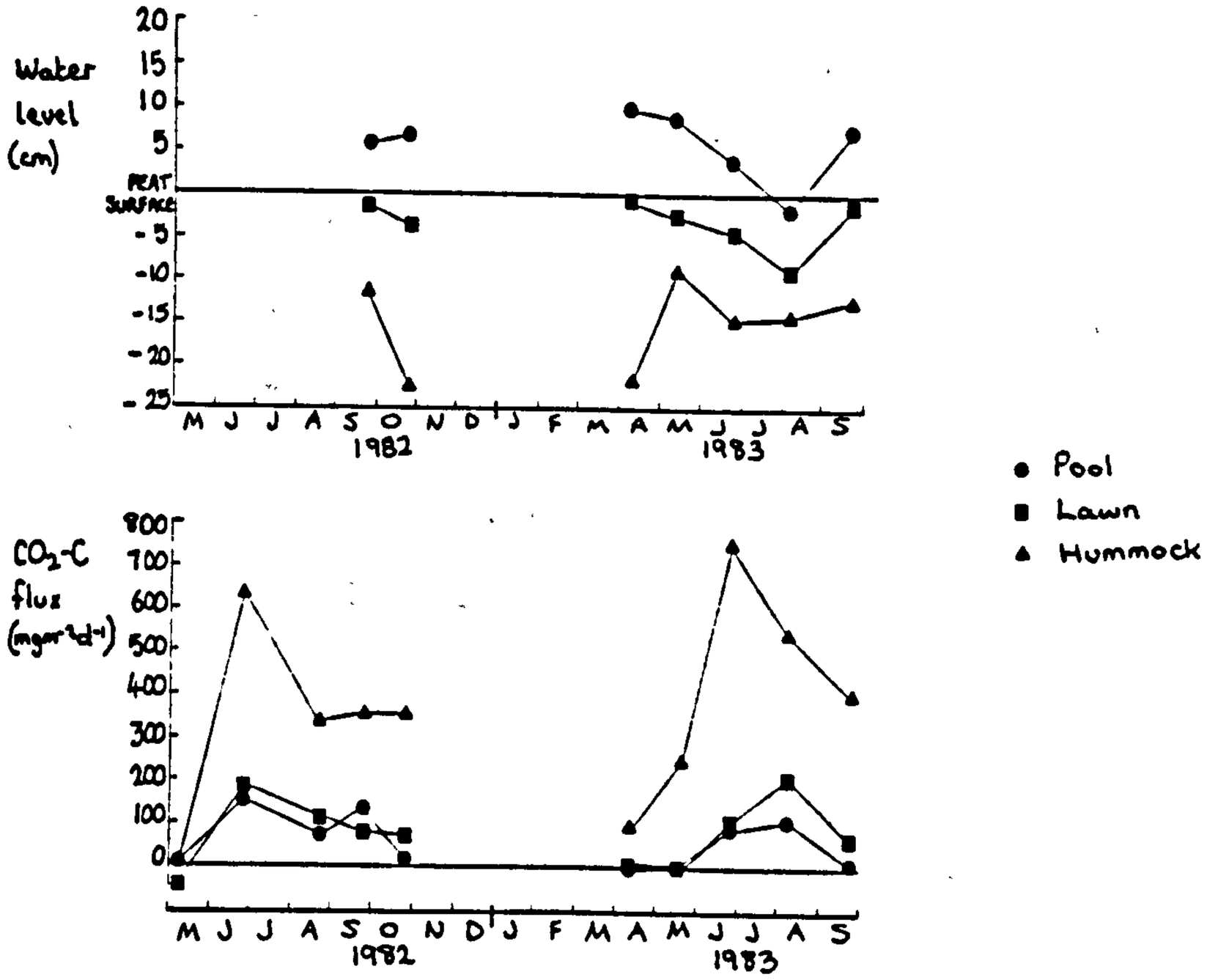
The mean rate of CO_2-C loss at CR was 382 ±87 mg m^{-2} d^{-1} (CD) and 90 ±28 mg m^{-2} d^{-1} (CW) at site 14, compared to 443 ±105 mg m^{-2} d^{-1} (CD) and 127 ±44 mg m^{-2} d^{-1} (CW) at site 16. Thus, there was more difference in carbon dioxide flux from the adjacent wet and dry areas within each site than there was between the fluxes from the wet or the dry areas of the two different sites. The approximately 20 cm difference between the mean wet and dry area water levels at site 14 gave a four-fold difference in carbon dioxide flux. At site 16, where the difference in mean water levels between wet and dry areas was about 10 cm, the difference in carbon dioxide flux was slightly less (3.5x). The differences in flux between the wet and dry areas were consistent, occurring on each field visit, but were more marked in the warmest months of the year.

d) Within microhabitats - field

Fig. 4.40 shows the mean fluctuations in CO_2-C flux above UP, UL and UH areas at MH. The water level changes are repeated from Fig. 4.27. Any correspondence (positive or negative) between water level

and CO_2-C flux seen in Fig. 4.40 is not consistent, either between microhabitats or within any one microhabitat with time. It is not possible to be certain about the cause of any such patterns in a

FIG. 4.40 Water level and carbon dioxide flux changes (uncut areas), Moor House, 1982-1983. Mean values of 3. Negative values indicate influxes.



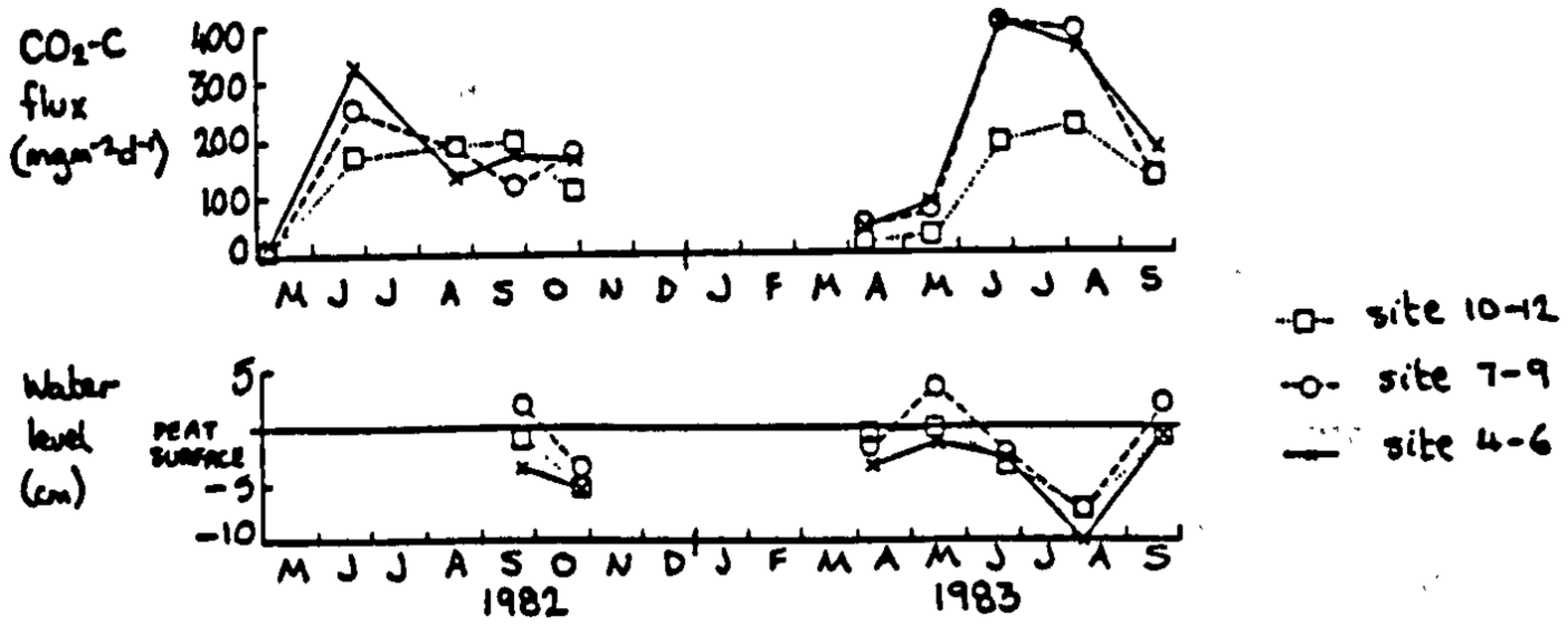
relatively small data set, but overall, a temperature effect best described the changes in flux at least between May and August. Analyses of variance, carried out on all MH data, revealed a significant TIME.HABITAT interaction ($p<0.001$, Table 4.15) for carbon dioxide flux. Between 25% (UP) and 30% (UL) of the variation in carbon dioxide flux above uncut pools and uncut lawns could be attributed to the effect of the water level alone ($p<0.01$, Table 4.17), and the r^2 value for all the uncut MH data clumped together was 0.35 ($p<0.001$). At CR water level accounted for about 50% of the variation in CO_2-C flux at sites 14 and 15 ($p<0.01$). This is in contrast to the non-significant r^2 values for methane flux and water

level at MH and CR. The results of a multiple regression approach to water level and temperature effects on CO_2-C flux are described below.

e) Between sites - field

The changes in CO_2-C flux and water levels at the three MH sites are shown in Fig. 4.41. There was no correspondence in rank order between site mean water level (Table 4.5) and CO_2-C flux. The site

FIG. 4.41 Site differences in water level and surface carbon dioxide flux, Moor House, 1982-1983



mean fluxes were 191 mg m^{-2} d^{-1}, 178 mg m^{-2} d^{-1} and 125 mg m^{-2} d^{-1} CO_2-C for sites 4-6, 7-9 and 10-12, respectively. The HABITAT.SITE interactive effect on water level was significant ($p<0.01$), but that on CO_2-C flux was not (Table 4.15). Methane flux gave a significant HABITAT.SITE interaction.

At CR there was also no correspondence between rank order of site mean water levels and CO_2-C fluxes (Table 4.13 and Fig. 4.20).

Thus, as for CH_4-C flux, there is no simple direct correspondence between site differences in CO_2-C flux and water level, but the two are correlated to some extent, at least for some sites. It seems likely that water level does play some rôle in the rate of CO_2-C loss from different parts of the bog, but that this is secondary to other effects; probably those of temperature and the more direct effect of surface vegetation type.

RELATIVE IMPORTANCE OF TEMPERATURE AND WATER LEVEL

As for methane, linear regression analyses were used in an attempt to clarify the relative importance of temperature and water level effects on carbon dioxide flux. The same independent variables were used (see Table 4.19), and a summary of the individual variable r^2 values (using CO_2-C flux as the dependent variable) have been included in Table 4.20, above. Appendix Kc gives the best fit (highest r^2 value) regression lines for CO_2-C flux on the most closely correlated single variables, and also the best-fit multiple regression equation.

Both the absolute and relative degree of (linear) correlation between CO_2-C flux and temperature and water level is variable with microhabitat and season. Overall, temperature accounts for more of the variation in CO_2-C flux the drier the habitat. Thus for pools, the temperature r^2 values were betweeen 0.08 and 0.25, compared with upwards of 0.69 for hummocks. The increase in importance of the temperature is accompanied by a decrease in the relative importance of the water level. In absolute terms water level is correlated with CO_2-C flux to a similar extent in pools (r^2=0.49) and lawns (r^2=0.54), and less so in hummocks (r^2=0.25).

The same general trends are evident when data collected during the warmer (>10°C) or cooler (<10°C) times of the year are considered.

In summary it can be said that temperature is more closely correlated (and water level less so) with CO_2-C flux the drier the habitat. The importance of both the temperature and the water level falls as the temperature drops in drier habitats, but increases in the wetter ones.

Tables 4.21 and 4.22 list the independent variables and the data sets used in the field CO_2-C flux regression analyses. It should be remembered that the following results refer to times of the year when both peat and air temperatures were above the annual mean of 5°C.

In general, in contrast to methane flux, that of carbon dioxide was more closely correlated with water level (r^2=0.28, $p<0.01$) than with temperature, as seen from the analysis of the complete MH and CR

data set and from nearly all the sub-sets of data (Table 4.23 and Appendix La). Further, for nearly all the sub-sets of data, the r^2 values for the water level and CO_2-C flux correlation were higher than for methane, whilst those for the temperature variables were lower (Table 4.23 and Appendix La). The water level and CO_2-C flux correlation coefficients were positive (negative for methane), indicating a decrease in CO_2-C flux with an increase in water level.

Water level fluctuations accounted for 35% of the variation in CO_2-C flux ($p<0.001$) at MH, with only pools and lawns returning significant r^2 values (0.25, $p<0.01$ and 0.30, $p<0.01$, respectively). At CR 26% ($p<0.01$) of the variation was attributable to water level changes, but only sites 14 and 15 gave significant r^2 values (0.47, $p<0.01$ and 0.52, $p<0.01$, respectively) (Table 4.23).

For all (full) data sets, the inclusion of temperature variables in addition to water level improved the correlation coefficients for CO_2-C flux considerably. The seven-variable multiple linear regression (spot air temperature; monthly maximum, minimum and mean Met. Off. air temperature; predicted peat temperature at -30 cm at time of record and for period since previous field visit, and water level) for MH and CR data clumped returned an r^2 value of 0.44 ($p<0.001$), compared with $r^2=0.28$ ($p<0.01$) for water level alone. The increase was larger at CR (from $r^2=0.28$, $p<0.01$ to $r^2=0.53$, $p<0.001$) than at MH (from 0.35, $p<0.001$ to 0.50, $p<0.001$) (Table 4.23) and thus it appears that at CR the temperature had a larger effect on CO_2 flux than at MH. This may reflect the wider range of microhabitat types (i.e. water levels) at MH, and the variation in flux associated with these. This is borne out by the r^2 values for the correlation between CO_2-C flux and the individual variables shown in Appendix La which are higher, and more significant, for water level ($r^2=0.35$, $p<0.001$) than for temperature (air temperature $r^2=0.12$, $p<0.05$) at MH, compared with CR where the water level was slightly less important (though significant) than the air temperature (water level $r^2=0.26$, $p<0.001$; air temperature $r^2=0.28$, $p<0.01$).

Including the temperature variables in the regression for MH pools gave a non-significant result. The inclusion of temperature variables in the regression for hummocks produced a significant r^2

value of 0.54 ($p<0.05$) which was not seen for water level effect alone. This is, apparently, in contrast to the relative degree of correlation with methane flux, where the temperature effect became more significant the *wetter* the habitat.

The same trends were evident from the individual CR site data sets such that although inclusion of temperature variables in the regression improved the r^2 values, in general, the effect was larger the drier the site, although only sites 15 and 17 returned significant r^2 values ($r^2=0.84$, $p<0.05$ and $r^2=0.97$, $p<0.01$, respectively). Appendix La also indicates that overall, the air temperature at the time of the gas sample record was the single temperature variable most closely correlated with CO_2-C flux. Only at site 16 (CR) were there consistent significant effects of the other temperature variables. Peat temperature was of very little importance, being insignificant in nine out of the eleven data sets tested, and the clumped MH and CR data set consistently returned lower r^2 values for the correlation between predicted peat temperatures and CO_2-C flux than between that and CH_4 flux (though none were significant).

EFFECT OF REMOVING THE GREEN MATTER

a) Seasonal effect

The corresponding section for methane, above, should be consulted for details of the analyses carried out. Fig. 4.42 compares carbon dioxide flux above uncut and cut control cores, the mean fluxes are

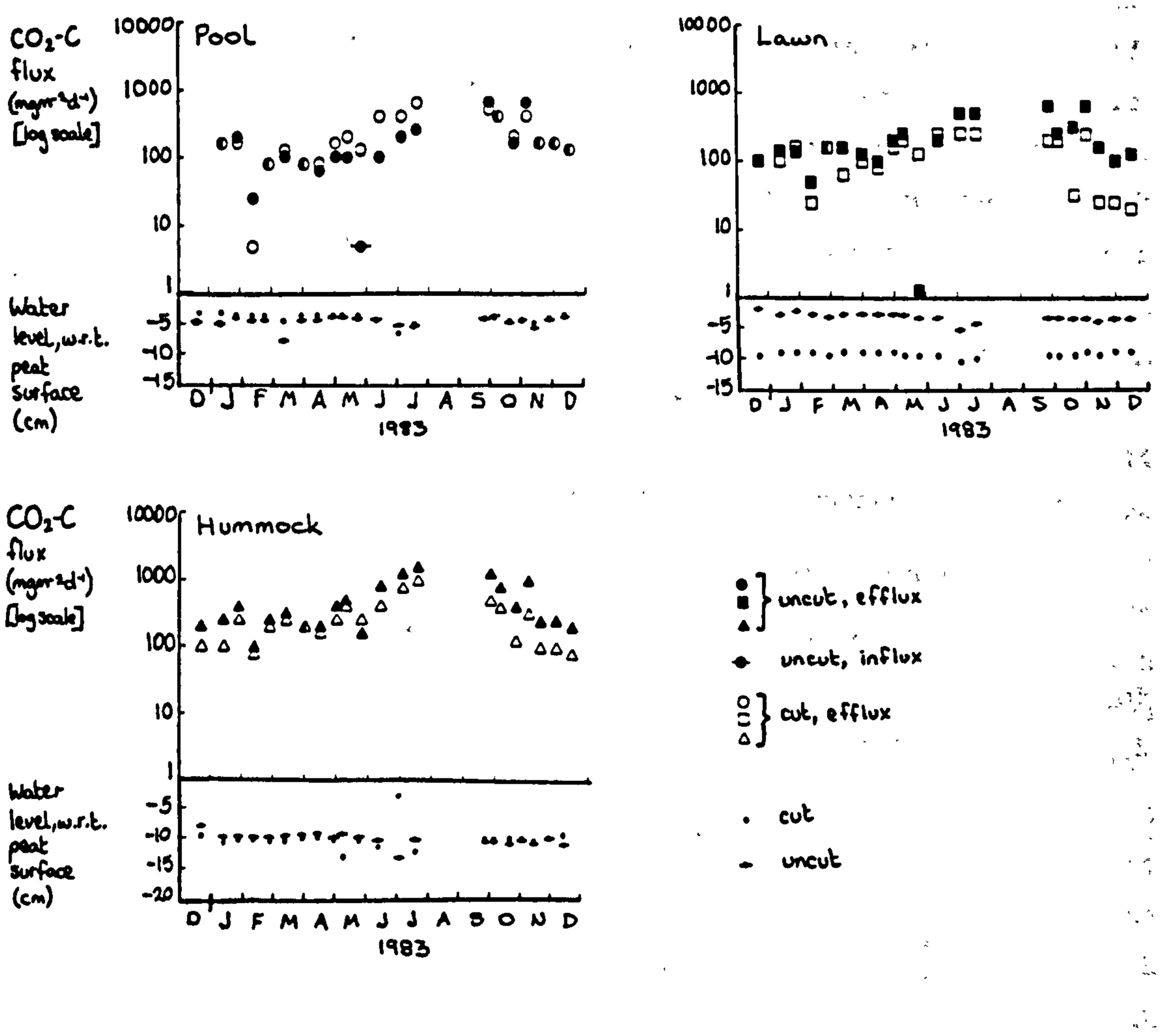
TABLE 4.36 Summary of carbon dioxide fluxes from uncut and cut control cores. Median of 2 values.

Exp^{tal} Stage	Pool		Lawn		Hummock	
	Uncut	Cut	Uncut	Cut	Uncut	Cut
	(mg m^{-2} d^{-1} CO_2-C)		(mg m^{-2} d^{-1} CO_2-C)		(mg m^{-2} d^{-1} CO_2-C)	
All*	196	232	235	137	512	291
I	103	101	131	98	250	163
II	149	322	270	213	777	522
III	322	284	323	110	585	241

* mean of stages I-III

given in Table 4.36, and Table 4.37 summarises the results of the Wilcoxon matched-pairs analyses for the carbon dioxide data. Seasonal peaks and troughs in CO_2-C flux occurred over cut cores, and coincided with those of intact cores. Overall, removing the green matter resulted in a significant decrease in the annual mean CO_2-C flux from hummocks (512 to 291 mg m^{-2} d^{-1}) and lawns (235 to 137 mg m^{-2} d^{-1}), but no significant change in that of pools (about 200 mg m^{-2} d^{-1}).

FIG. 4.42 Comparison of surface carbon dioxide flux from uncut and cut control cores



The effect of removing the green matter was more consistent the drier the microhabitat. Thus, above hummocks the uncut cores consistently showed a higher CO_2-C flux than the cut cores, as did the lawns, but here the absolute difference appeared to vary seasonally.

In contrast, the effect on pools appeared to vary in direction as well as in magnitude, differences being smaller at the cooler times of the

TABLE 4.37 Summary of Wilcoxon matched-pairs analyses, comparing uncut and cut control core carbon dioxide fluxes (within microhabitats).

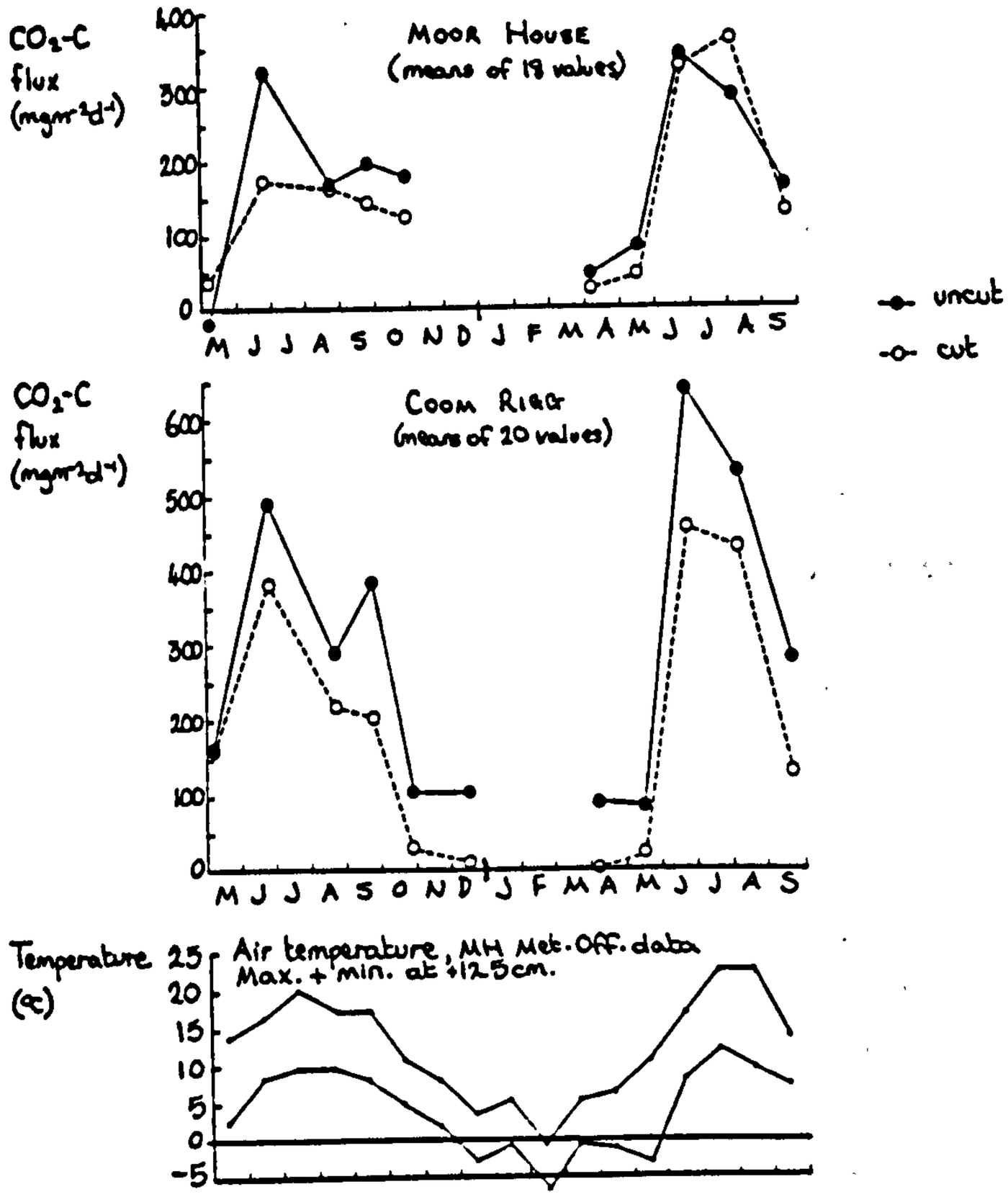
Expt^{al} stage	Pool	Lawn	Hummock
All	U = C	U > C	U > C
I	U = C	U > C	U > C
II	C > U	U = C	U > C
III	U = C	U > C	U > C

Significant results (i.e. $p<0.05$) shown by >
Non-significant comparisons shown by =

year and cut area fluxes tending to be lower than uncut area ones, whereas in summer the differences were larger and cut areas evolved more CO_2. It is possible that these results are, at least in part, a manifestation of the differences in the ratio of photosynthetic : non-photosynthetic material in the three microhabitat surface vegetation types, which will affect both the absolute and relative amount of net CO_2-C produced.

The seasonal changes in CO_2-C flux from uncut and cut areas at MH and CR and the corresponding monthly mean (Met. Off.) maximum and minimum air temperatures are shown in Fig. 4.43. As for methane, the general seasonal trends in carbon dioxide efflux were unaffected, except to the extent that the larger deflections in the uncut area curves in Fig. 4.43 were damped in the cut area plots. Peaks and troughs in carbon dioxide flux from uncut and cut areas coincided almost exactly. Cut cores at both sites apparently reflected the higher summer temperatures in 1983 in higher fluxes. Also as for methane, removing the green matter reduced the CO_2-C flux, though the significance of the difference varied between Sites, according to analyses of variance (CUT effects; MH non-significant, Table 4.15; CR $p<0.001$, Table 4.16). Overall, at MH the flux was reduced from 176 mg m^{-2} d^{-1} to 153 mg m^{-2} d^{-1} (13%) when the green matter was removed, compared with a drop from 278 to 184 mg m^{-2} d^{-1} (34%) at CR, Tables 4.9 and 4.13. This represents a drop in CO_2-C flux of

FIG. 4.43 Seasonal carbon dioxide flux from uncut and cut areas, Moor House and Coom Rigg, 1982-1983



0.8 mg m^{-2} d^{-1} g^{-1} dry weight of biomass removed at MH, and 1.7 mg m^{-2} d^{-1} g^{-1} dry weight at CR. Thus, removal of the green matter resulted in a smaller proportional drop in CO_2-C flux than was the case for CH_4-C, but in absolute terms the loss of CO_2-C was affected to a greater extent.

The effect of cutting varied between years and sites, being more variable both within and between seasons at MH than at CR.

b) Effect of the water level

The mean CO_2-C flux from uncut control cores for the experimental period increased ($p<0.01$) with increasing dryness of the microhabitat, from 196 mg m^{-2} d^{-1} CO_2-C for pools to 235 mg m^{-2} d^{-1} for lawns and

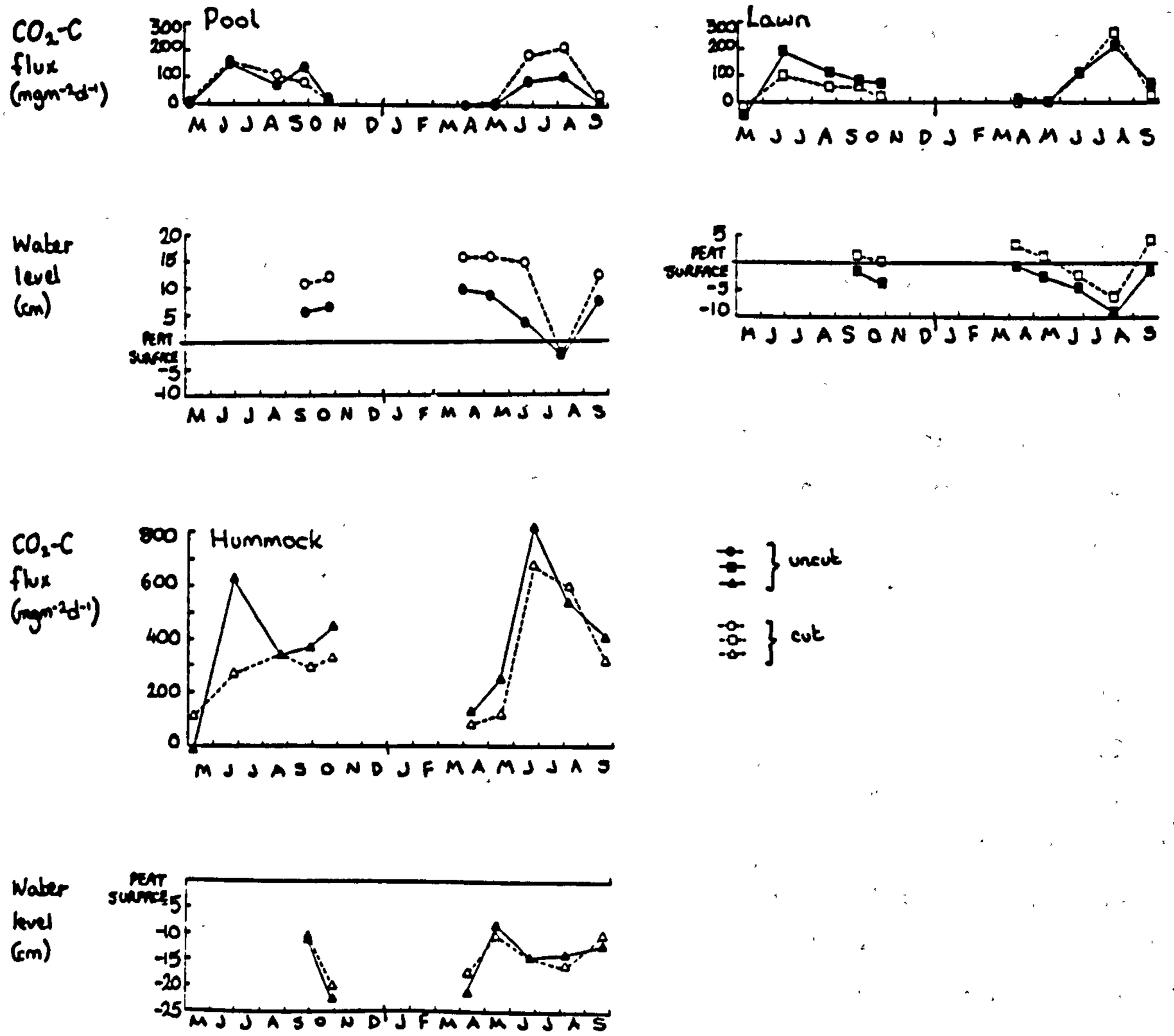
512 mg m^{-2} d^{-1} for hummocks (Tables 4.35 and 4.36). The differences were consistent at each stage of the experiment and increased in size and significance in the summer months (stage II): the difference between hummock and lawn flux increased 2- to 3-fold, and that between lawns and pools between 1.3- and 2-fold.

Comparing these results with those from cut control cores (Table 4.36), it is clear that the response to removal of the green matter was different in each microhabitat. Cutting hummock cores resulted in a drop in the annual mean CO_2-C flux of 221 mg m^{-2} d^{-1}, and for lawns a drop of 98 mg m^{-2} d^{-1}. There was an apparent increase in flux above cut pools (of 36 mg m^{-2} d^{-1}), but this was not significant according to a Wilcoxon matched-pairs analysis. The differences between uncut and cut hummocks and lawns were consistent (in direction) throughout the year, so that removal of green matter had no effect on their relative importance for CO_2-C loss, the flux being higher from hummocks whether intact or cut. In contrast, the effect of removing the green matter from pools was seasonal, there being a reduction in CO_2-C flux from cut pools in autumn through to spring, but a significant (two-fold) increase in flux in summer (stage II, April to July). As a result, the importance of the cut pool microhabitat as a source of CO_2-C efflux relative to that of cut lawns and hummocks varied with season, in contrast to the consistent relationship of intact pools, lawns and hummocks. Over the year as a whole, and in the autumn (September to December) cut pools evolved more CO_2-C than either lawns or hummocks, but for the rest of the year there was no significant difference between the CO_2-C flux from pools and lawns, and that of hummocks was greater than both.

The mean dry weight of green biomass removed initially from the lawn cores was about 39 g, and the corresponding drop in the annual mean CO_2-C flux was 98 mg m^{-2} d^{-1}, compared with a 221 mg m^{-2} d^{-1} drop for hummocks, or more than twice that of lawns for a similar dry weight of green matter removed (≃40 g).

Fig. 4.44 illustrates the differences in carbon dioxide flux from uncut and cut microhabitats at MH; the mean efflux rates for the study period were given in Table 4.29, above.

FIG. 4.44 Seasonal changes in water level and carbon dioxide flux in uncut and cut microhabitats, Moor House, 1982-1983. Negative values indicate an influx.



The effect on carbon dioxide flux of the removal of the green matter was less consistent between microhabitats than was the case for methane. An analysis of variance returned a significant ($p<0.01$, Table 4.15) result for the HABITAT.CUT interaction on CO_2-C efflux (cf non-significant for methane).

Removal of the green matter from pools resulted in an increase in CO_2-C efflux of 25 mg m^{-2} d^{-1} (42%), or 10.4 mg m^{-2} d^{-1} g^{-1} dry weight removed. Lawn efflux fell by 19 mg m^{-2} d^{-1} to 61 mg m^{-2} d^{-1} (24%, or 0.7 mg m^{-2} d^{-1} g^{-1} dry weight removed). Hummocks showed the largest absolute change (drop) in CO_2-C efflux, of 76 mg m^{-2} d^{-1}, to 314

mg m^{-2} d^{-1} (19%, or 1.2 mg m^{-2} d^{-1} g^{-1} dry weight of material removed).

Cut control and experimental core CO_2-C fluxes are compared in Fig 4.45 for each of the three microhabitats; the mean fluxes for the experimental cores for each stage of the garden experiment are shown in Table 4.38, and may be compared with the equivalent values for the controls in Table 4.36.

TABLE 4.38 Summary of mean carbon dioxide (CO_2-C) fluxes from uncut and cut experimental cores (mg m^{-2} d^{-1}).

	Pool		Lawn		Hummock			
					Experimental groups			
					H5,H7	H10,H11	H2,H4	H6,H9
Exp^{tal} stage	Uncut	Cut	Uncut	Cut	Uncut		Cut	
All*	306	262	405	244	553	504	351	302
I	128	107	122	88	256		148	168
II	228	372	526	368	911	727	713	274
III	551	323	626	318	587	597	244	478

* mean of stages I-III

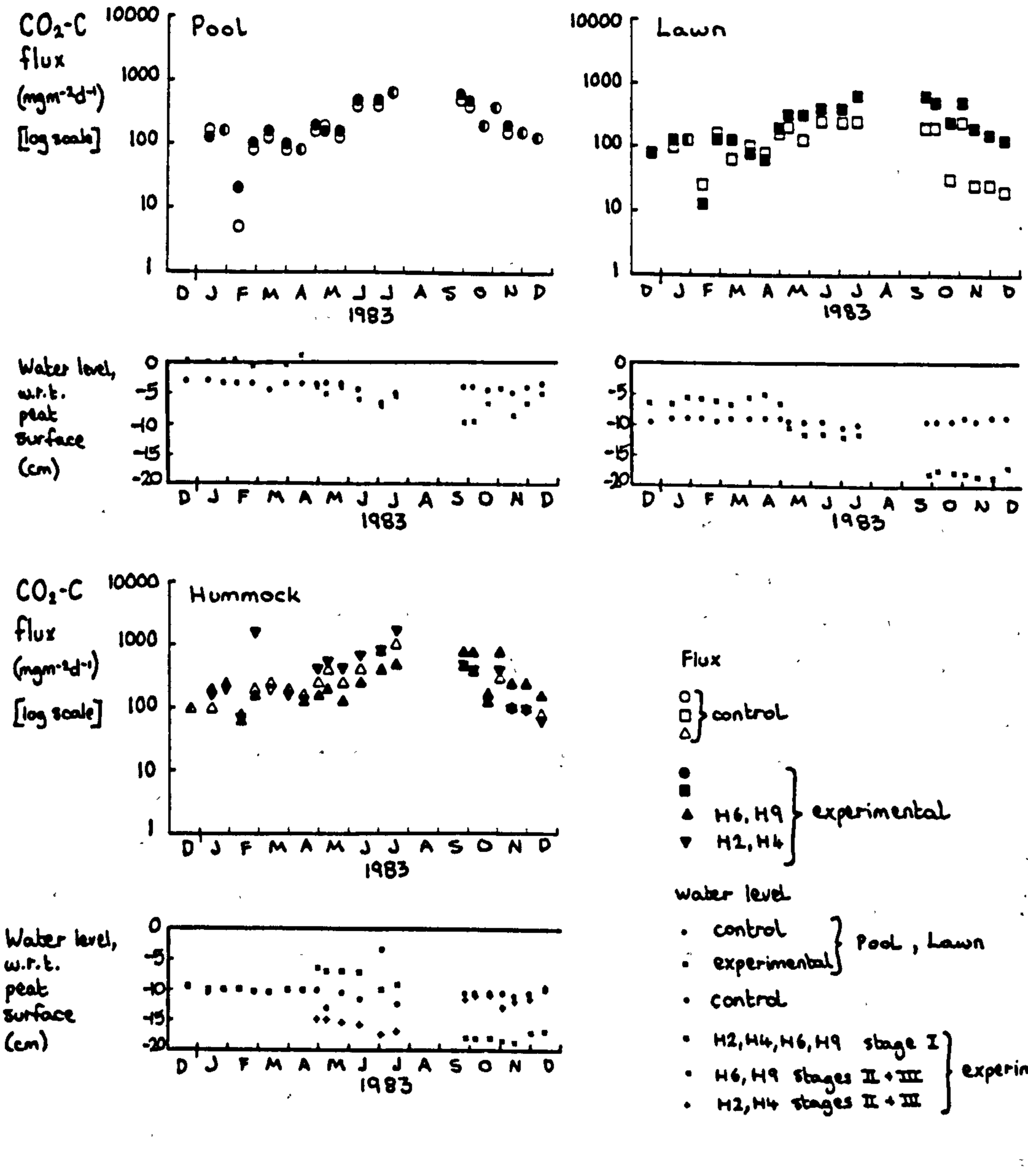
Results from intact cores had suggested that water level might play a small rôle, subsidiary to temperature, in pools and lawns in determining the rate of CO_2-C flux. There was little such evidence for hummocks. From Fig. 4.45, however, it would appear that water level does affect CO_2-C flux, at least after removal of the green matter. This suggests that under normal circumstances the temperature effect on the O_2:CO_2 balance swamps any small effect of water level on CO_2-C flux from the underlying respiring, non-photosynthetic system. The water level effect on lawn CO_2-C flux from intact cores is still evident (Fig. 4.45) when the green matter is removed.

The differential effect on CO_2-C flux of removing the green matter from the three microhabitats is clear, but the standard errors of the means in Table 4.29 give overlapping 95% confidence limits for the uncut and cut area means within each of the three microhabitats. This presumably results from the seasonal effect of cutting (TIME.CUT interaction, $p<0.05$, Table 4.15), clear in Fig. 4.44, in which

differences tend to be larger in warmer weather, and the relative flux of cut and uncut areas is reduced, or may even be reversed, in winter.

As for methane, there was no significant difference in the effect of cutting on CO_2-C flux between the three MH sites (Tables 4.15 and

FIG. 4.45 Surface carbon dioxide flux from cut control and experimental garden peat cores, December 1982 - December 1983



4.31) but a highly significant difference ($p<0.001$) at CR (Tables 4.13 and 4.16). There was no correspondence between the proportional drop in CO_2-C flux and the dryness of the site or the size of the apparent increase in water level in the cut areas. However, the rank order of increasing dryness of site and increasing rate of reduction in efflux per gram dry weight of material removed did coincide.

c) Relative importance of temperature and water level

As for the uncut cores, regression analyses were carried out on the cut cores, and the results compared to see if removal of the green matter had any effect on the relative importance of the temperature and water level on CO_2-C flux. The r^2 values for the CO_2-C flux from cut cores on each of the individual variables are shown in Table 4.33; the individual variable and multiple regression equations which gave the highest r^2 values for each data set are shown in Appendix Kd. These results should be compared with those for the uncut cores, in Table 4.20 and Appendix Kc.

In contrast to the apparent decline in the influence of temperature on the methane flux from cut cores, the influence of temperature on carbon dioxide flux increased, absolutely and in relation to that of the water table, when the green matter was removed. In this case the increase in the effect decreased with the dryness of the microhabitat (cf effect on CH_4-C flux). Thus, the r^2 values for the pool temperature variables changed from about 18% to 65% on being cut, lawn temperature r^2 from 52% to 60% and hummock tempearature r^2 from 71% to 73%. The same temperature variables were important in uncut and cut cores; in each microhabitat the air temperature at sampling was the least important and the median two day interface temperature the most influential.

Conversely, in absolute (and relative, to temperature) terms the correlation between water level and CO_2-C flux decreased in the order CP ($r^2=0.34$), CL ($r^2=0.26$), CH ($r^2=0.23$). In the intact cores the water level r^2 values were about 200%, 100% and 30% those of the temperature r^2 values for pool, lawn and hummock, respectively, whereas in cut cores the corresponding percentages were about 50%, slightly less than 50%, and about 30%. These effects were also seen

in the multiple regression equations, for which the r^2 value was enhanced by less than 0.1 for all cut microhabitat equations when water level terms were introduced, but were increased by more than 15% in UP and UL equations, and by 7% in UH regressions.

In general, the regression equations accounted for more of the variation in CO_2-C flux from cut cores than from intact ones. In all cut cores the most important temperature variable was the mean peat temperature since the previous sample, compared to the air or interface temperature for intact cores.

The relative importance of water level and temperature influences changed for cut areas compared with uncut. Although no individual temperature variable r^2 value for any of the data sets tested was significant, there was an increase in almost all, which is unlikely not to be real. Uncut area data groups which returned significant water level r^2 values gave much lower r^2 values for the temperature variables, but cut data groups showed absolute and relative increases in the temperature correlation relative to that of the water level.

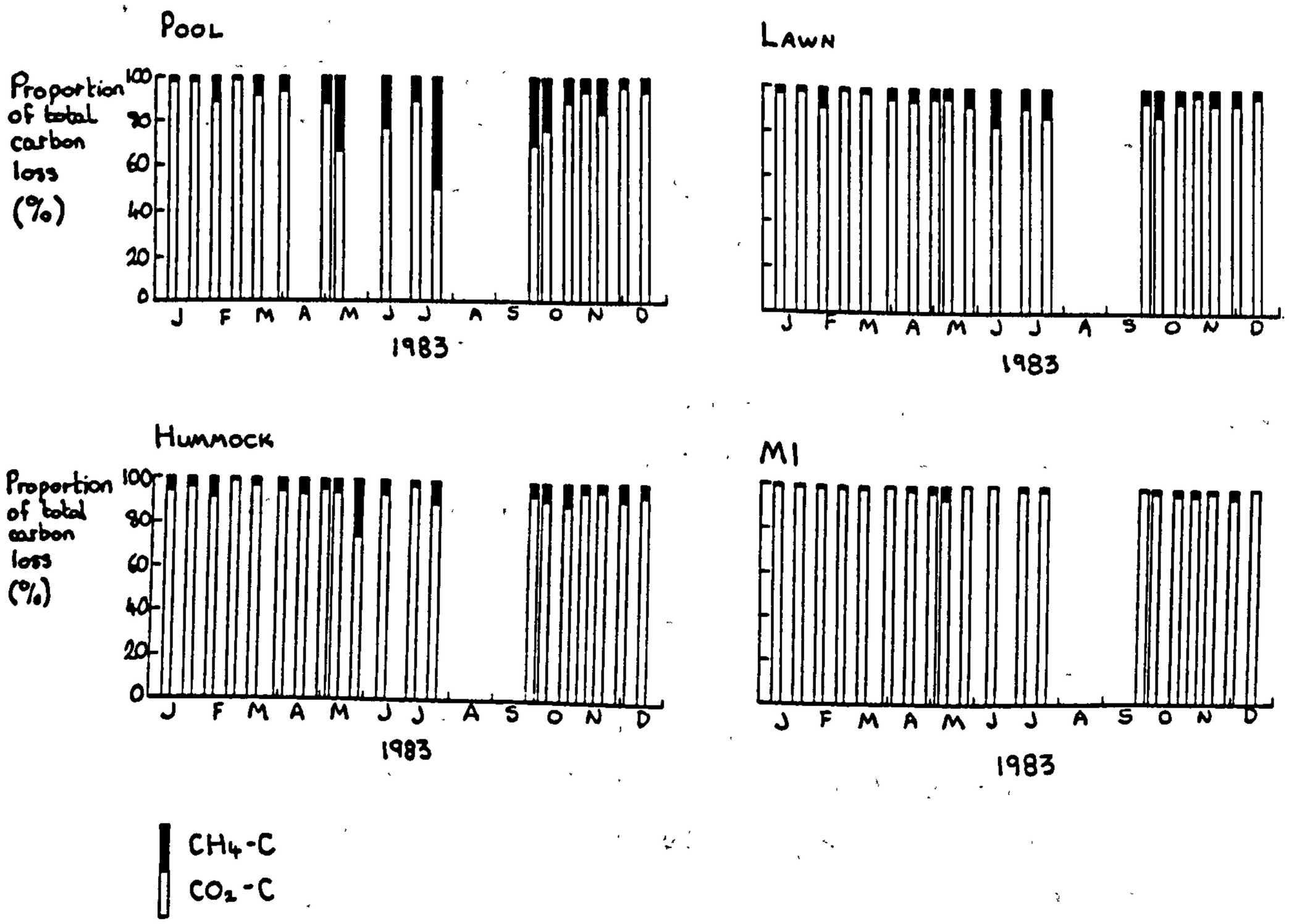
The importance of the air temperature appeared to diminish for cut areas the drier the habitat. This is in contrast to the trend seen above uncut areas, and corresponds to that seen for methane. Except at site 14, the peat temperature variables gave lower r^2 values than the air temperatures, but of the four predicted temperatures that based on the Met. Off. data equation for the day of sampling gave, consistently, the highest. At CR and MH the overall increase in the air and peat temperature r^2 values was roughly the same; about two-fold at MH and slightly less than this at CR. Overall, MH and CR data clumped, air temperatures accounted for just over 30% of the variation in carbon dioxide efflux, and peat temperatures just less than 30% (cf uncut data where both air and peat temperatures accounted for about 17% of the variation). Hence, the multiple regression equations for the cut data were significantly improved over those of the uncut areas. Coefficients of determination for the seven-variable multiple regression increased by 10-20%, such that overall the variables accounted for 62% ($p<0.001$) of the variation (65% at MH and 69% at CR), cf 44% (55% and 53% at MH and CR, respectively) for intact area

data. Only at site 16 was the regression non-significant (both uncut and cut).

4.2.6 RELATIVE METHANE AND CARBON DIOXIDE EFFLUX

Using the 1983 uncut garden data a median flux was calculated for methane and carbon dioxide for each microhabitat and hence the total carbon flux for each microhabitat was obtained, assuming this to be the sum of the two. The proportion of the total carbon loss at each sampling attributable to each gas was calculated for the controls and for M1, and the results are shown in Fig. 4.46

FIG. 4.46 Relative contribution of methane and carbon dioxide to total carbon loss from intact garden cores and Minibog



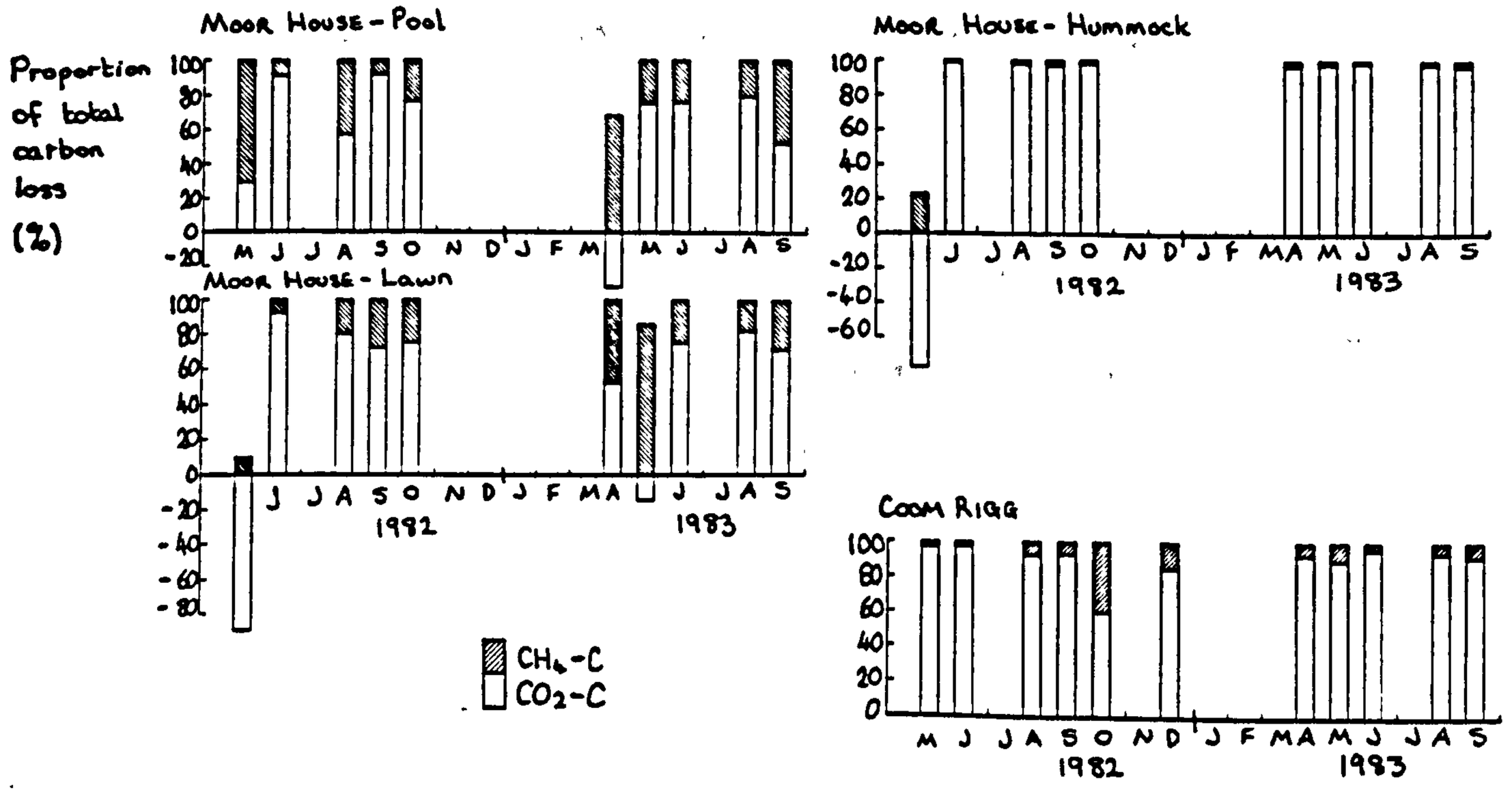
SEASONAL EFFECT

The contribution which surface methane flux makes to total carbon loss appeared somewhat erratic, probably partly due to there being only two cores on which each estimate was based. Despite this, it is clear that as temperatures increased in summer, methane contributed relatively more, the trend tending to become less marked the drier the habitat. Thus in uncut pools methane accounted for up to 50% of total carbon loss, in July, with a mean annual contribution of 14%. There was a slight summer increase in the proportion of methane from lawns, the maximum being 17% in June. The hummock maximum occurred yet earlier in the year; 26% in May. The annual mean methane contribution from lawns and hummocks was 6% and 7%, respectively, compared with 2%, apparently, from the minibog. There was an increase from about 2% to 10% in the proportion of methane in February from all the control cores, possibly a reflection of a slowing down of diffusion near the surface in response to the very low air temperatures during that period. It may appear contradictory that the CH_4 percentage was higher when the air temperatures were low, *and* during the summer months, but in both cases the peat temperature was warmer; relatively so in February, compared with the air temperature, and absolutely warmer in summer than at other times.

Turning to the results from the field sites, the 1982 and 1983 data from the uncut MH and CR sampling areas were used to calculate the proportion of the total carbon loss attributable to CH_4 and CO_2 on each visit. Microhabitats were treated separately at MH. The results are shown in Fig. 4.47.

As for the garden results, those from the field were somewhat erratic, to the extent that those from MH were inconclusive, although those from CR suggested that a higher proportion of carbon was lost as methane in the warmer months. Overall, proportional loss of methane was greater in the field, but the difference varied between microhabitats: field UP 'annual' mean CH_4-C proportion was 34% compared with 14% in the garden; that of UL 30% compared with 6%; and for UH areas 2% compared with 7%.

FIG. 4.47 Relative contribution of methane and carbon dioxide to total carbon loss from uncut sampling areas at Moor House and Coom Rigg. Negative values indicate an influx.



On four field visits, all in the early part of the season (April and May), carbon dioxide flux was negative, and on three out of four of these occasions, this coincided with the maximum CH_4-C proportional loss.

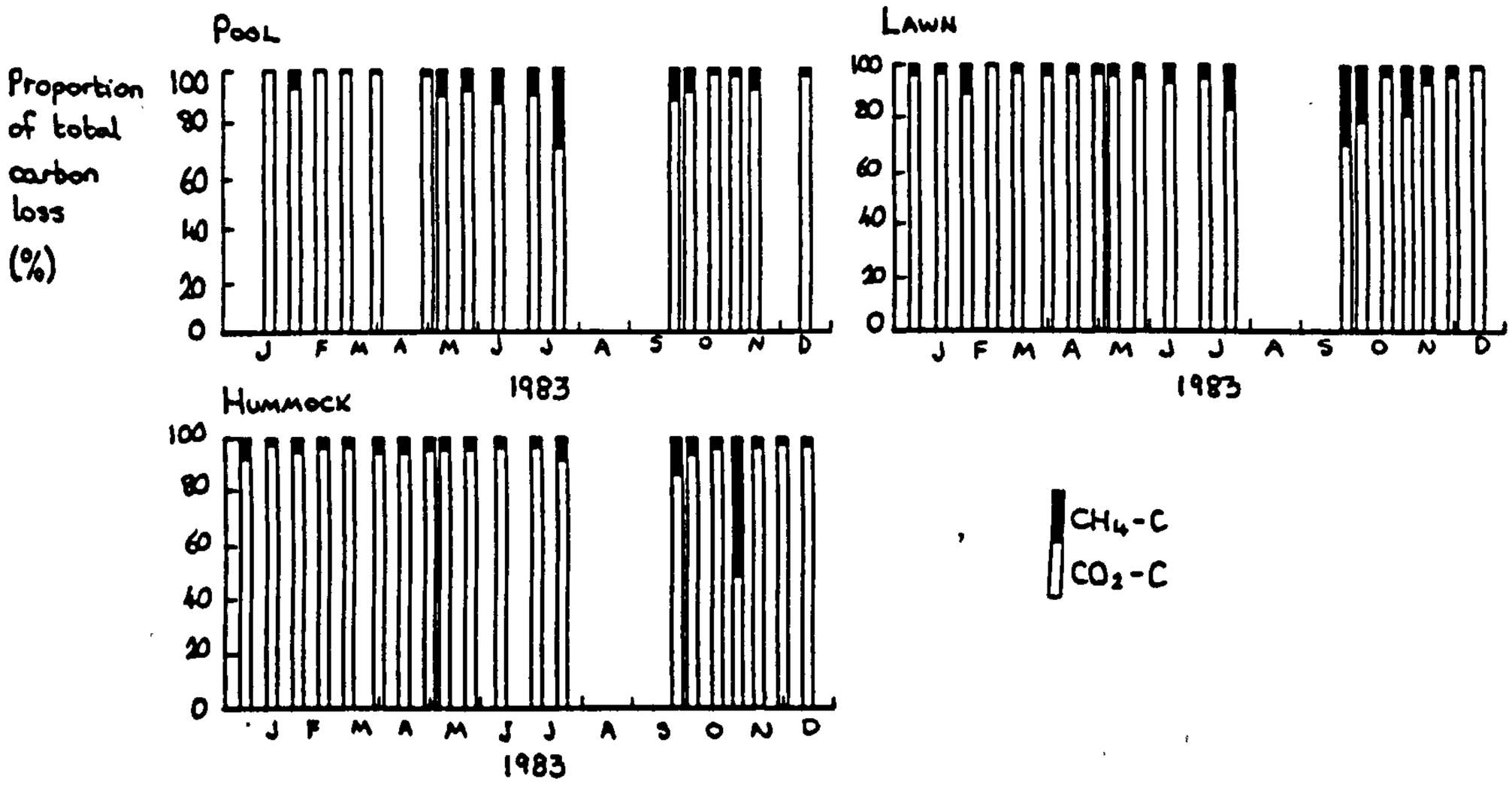
EFFECT OF REMOVING THE GREEN MATTER

The proportional loss of CH_4-C and CO_2-C from garden cut control cores is shown in Fig. 4.48.

The cut pool cores showed the same increase in the proportion of methane in spring and early summer, peaking in the mid-July record, as did the uncut cores, but the absolute proportions were lower. This is a direct consequence of a decrease in the absolute methane flux from cut cores compared to uncut cores, and a simultaneous overall increase in the carbon dioxide efflux.

The cut lawn cores also showed the seasonal increase in the proportion of methane but the peak was higher than for the uncut lawn cores, and occurred later. It accounted for about 30% of the total carbon flux in late October compared to a maximum of less than 20% in

FIG. 4.48 Relative contribution of methane and carbon dioxide to total carbon loss from cut garden cores



June-July in the uncut cores. This increase in the proportion of methane compared to that in uncut lawn cores resulted because although both methane and carbon dioxide flux above cut lawns was reduced, the decrease was about 44x greater for carbon dioxide than for methane.

Removal of the green matter from hummock cores gave the same response as in lawns; the peak in the methane proportion occurred later (November compared to May) and was much larger (51% compared with 26%). The November peak is large and sudden, and may be erratic. The September value (14%) is probably a better representation of the seasonal peak.

The relative contribution of methane and carbon dioxide to the total carbon loss from MH cut sampling areas is shown in Fig. 4.49. Overall, cutting resulted in a reduction of the proportional CH_4-C loss from all the microhabitats at MH, from 29%, 31% and 2% of total carbon loss for intact pools, lawns and hummocks, respectively, to 18%, 16% and 0.2% on cutting. Thus, the proportional decrease was larger the drier the habitat.

Relative Methane and Carbon Dioxide Efflux

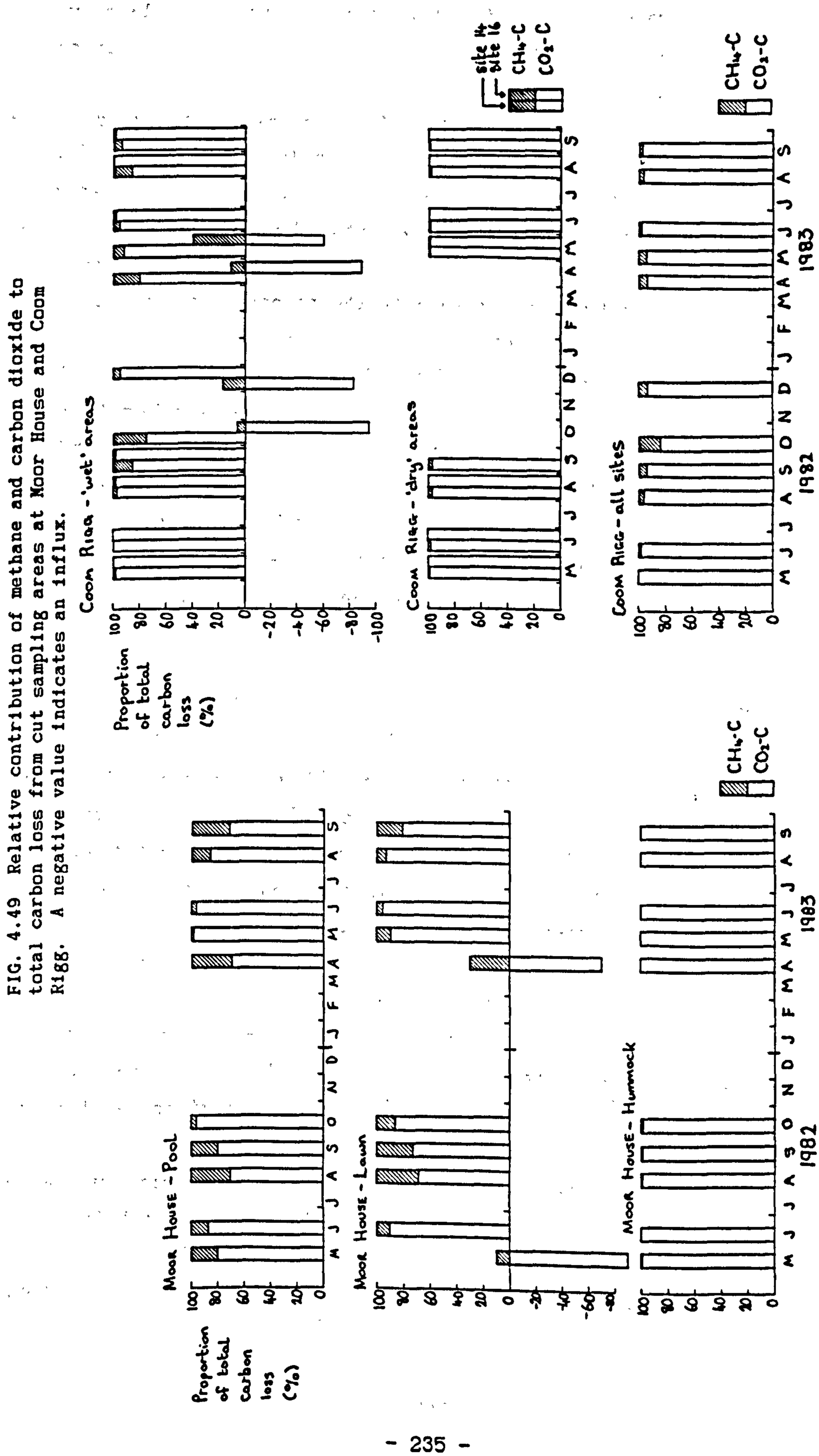


FIG. 4.49 Relative contribution of methane and carbon dioxide to total carbon loss from cut sampling areas at Moor House and Coom Rigg. A negative value indicates an influx.

Seasonal trends in the CH_4-C proportion in pools and lawns varied considerably between the two years of the study, cut hummocks showed no seasonal trends in either year.

At CR, at all sites except site 17, removal of the green matter resulted in a decrease in the CH_4-C proportion of the total carbon mass lost. The mean site decreases in the mass flux ratio of methane:carbon dioxide, ranged between 14% (from 0.07:1 to 0.06:1 at site 15) to 76% (from 0.02:1 to 4.8×10^{-3}:1 at site 16). There was no correspondence between the change in the proportional loss of CH_4-C and the mass of material removed.

Both MH and CR results from cut areas showed an influx of CO_2-C at some time during the study. All such records were confined to April and May at MH, and to the cooler period between October and May at CR. Influxes of CO_2-C occurred only into cut lawns at MH, compared to all three intact microhabitats. At CR CH_4-C influx into cut areas was similarly confined to the wet ones. There was no consistent correspondence at either MH or CR between CO_2-C influx and maximum proportional CH_4-C loss.

4.2.7 OXYGEN INFLUX

Oxygen influx was monitored in the same way as that of methane and carbon dioxide, the main purpose of this was to allow a check of sample contamination, but also to obtain information about oxygen-carbon dioxide balances. In the event, the oxygen results were less reliable than had been hoped, not least because an accurate calibration was not possible until late into the study. Furthermore, the sensitivity of the GC was much reduced during the elution of O_2 and N_2, in order to obtain measureable, on-scale, peaks, but was subsequently increased for CO_2. Hence, small changes in O_2 concentration, large enough to have a noticeable effect on respiration and measured CO_2 flux, were not detectable.

Notwithstanding these considerations, the same analyses were carried out for O_2 as for CH_4-C and CO_2-C, in order to highlight any consistent, major features. The detailed results of the analyses are not reported, since individually they are not indicative. However,

taken together, certain trends were suggested, though these were by no means conclusive. They are included in the summary results (Tables 4.11 and 4.12).

The 'annual' mean O_2 oxygen influx for uncut pools, lawns and hummocks, respectively, was -1370, -940 and -3440 mg m^{-2} d^{-1}, and the overall mean flux for MH (uncut areas) was -1920 mg m^{-2} d^{-1}. At CR the 'annual' mean oxygen flux for the uncut areas was -2980 mg m^{-2} d^{-1}.

A seasonal pattern of O_2 influx was evident from the field results (increased flux in the warmer periods), but was less clear cut than for CH_4 and CO_2. Indeed, in the garden cores it was rather unclear, whether or not the green matter had been removed, although a finer analysis of garden experimental results showed some evidence of an increase in O_2 uptake, which lagged behind that of methane.

The field site results indicated an inverse correspondence between water level and O_2 influx which varied between microhabitats (and sites), and this was clearer when the green matter had been removed. However, it was apparent from both the field and the uncut garden core results that the differences were not solely the effect of the water level, but were compounded by the effect of temperature on different vegetation types. It was beyond the scope of this study to disentangle the details of their respective effects. Overall, water level alone accounted for 32% of the variation in O_2 uptake (cf 37% for CO_2-C efflux and 28% for CH_4-C efflux), and temperature variables for between 34% (air) and 47% (interface). Of the temperature variables, there was no consistency as to which was most closely correlated with O_2 uptake, either between microhabitats or seasonally. In general, oxygen uptake was less fully explained in terms of water level and temperature variables than was methane or carbon dioxide efflux. In summary, though, the results suggested that large changes in water level were associated with the gross differences in oxygen uptake but temperature was more important in explaining the smaller changes in flux which were recorded seasonally within a single sampling area type (of microhabitat).

Removal of the green matter had no clear effect on O_2 influx, as it had on CH_4 and CO_2 fluxes.

4.2.8 RELATIVE CARBON DIOXIDE AND OXYGEN FLUX

The large disparity in O_2 and N_2 compared with CO_2 concentrations in samples, and the consequent inability to measure O_2 and CO_2 with the same degree of accuracy, should be borne in mind when considering the RQ values presented in this section.

It is convenient to consider the results for the cut sampling areas first, since respiratory quotients (the molar ratio of CO_2 evolved to O_2 taken up over a given period) are less ambiguous without the complication of photosynthetic activity.

The respiratory quotients (RQs) for the MH cut sampling areas and those of sites 14 and 16 at CR are shown in Table 4.39.

The majority of RQ values were <1.0, indicating an excess of O_2 taken up over CO_2 evolved. The mean values for each of the MH microhabitats over the two study periods were 0.09 (CP), 0.05 (CL) and 0.10 (CH). It is not clear why the values are so low, but the microhabitat differences may provide a clue insofar as cut lawns appear to show the largest excess of O_2 uptake over CO_2 efflux. *Eriophorum angustifolium* was the dominant vascular species growing in lawn areas, and this is known (Armstrong 1964) to allow the movement of O_2 downwards and out from its roots, where it could conceivably oxidise H_2S, for example. The values in Table 4.39 are rather variable, but there is a slight tendency for an increase in RQ over the first half of the season, and a subsequent decline towards winter, suggesting an increase in CO_2 production (or evolution only) relative to O_2 consumption in the earlier part of the season. Part of this increase in CO_2 flux may be a result of CH_4 oxidation, fuelled by other than O_2.

The RQ values for the uncut field sampling areas are shown in Table 4.40. As for the cut areas, almost all the values were <1, but there was a clear increase with dryness of habitat (presumably associated with the corresponding proportional decrease in photosynthetic biomass), which was less clear when the green matter had been removed. There were exceptions to this, notably in June and September 1982, when mean RQ values were generally >1, and decreased with dryness of the habitat. The reasons for these high values are

Relative Carbon Dioxide and Oxygen Flux

TABLE 4.39 Respiratory quotients for cut areas at Moor House and Coom Rigg (sites 14 and 16). Moor House values are means of 3.

Date	Moor House			Coom Rigg				
					CW		CD	
	CP	CL	CH	Site	Site mean	Date mean	Site mean	Date mean
May 82	*	*	0.7	14	0.8	0.6	0.4	0.4
				16	0.4		0.4	
Jun 82	2.5	2.0	0.8	14	1.3	1.3	0.9	1.1
				16	1.2		1.2	
Aug 82	0.2	0.1	0.1	14	0.3	0.2	0.3	0.3
				16	0.1		0.3	
Sep 82	0.3	5.0	0.0	14	0.1	0.1	0.2	(0.2)
				16	0.1		-	
Oct 82	0.04	0.02	0.2	14	0.1	(0.1)	-	-
				16	*		-	
Dec 82	-	-	-	14	*	(<0.1)	-	-
				16	<0.01		-	
Apr 83	<0.01	*	0.03	14	<0.01	(<0.1)	-	-
				16	*		-	
May 83	0.03	<0.01	0.1	14	0.04	(<0.1)	0.1	0.1
				16	*		0.1	
Jun 83	0.3	0.2	0.5	14	0.1	0.2	0.2	0.3
				16	0.2		0.4	
Aug 83	0.3	0.3	0.6	14	0.2	0.3	*	(0.3)
				16	0.4		0.3	
Sep 83	0.08	0.05	0.2	14	*	0.3	0.2	0.5
				16	0.2		0.7	

* RQ negative
Figures in parentheses are based on data from one site only

Mean water levels (cm)

CP	CL	CH		CW	CD
+10.7	+0.4	-14.1	Site 14	+6.2	-14.0
			Site 16	+2.9	-7.0

not clear; indeed, they suggest that the uptake of oxygen was not keeping pace with respiration and if this were so, an alternative oxygen source must be sought to support continued aerobic respiration. High RQ values are indicative of anaerobiosis.

TABLE 4.40 Respiratory quotients for uncut areas at Moor House and Coom Rigg. Means of 3 (MH) and 5 (CR).

	MH			CR
Date	UP	UL	UH	U
May 1982	*	*	*	0.5
Jun 1982	2.5	2.5	1.0	1.2
Aug 1982	0.1	0.2	0.4	0.4
Sep 1982	2.5	2.0	0.6	0.3
Oct 1982	0.02	0.3	0.2	0.03
Dec 1982	-	-	-	0.01
Apr 1983	*	0.04	0.04	0.04
May 1983	0.004	*	0.2	0.1
Jun 1983	0.2	0.3	0.6	0.3
Aug 1983	0.2	0.3	0.5	0.6
Sep 1983	0.03	0.08	0.3	0.3

* RQ negative

On several occasions the RQ was not calculated (indicated by an asterisk (*) in the Tables) because either net CO_2 flux was into the peat or net O_2 flux was outwards, giving negative RQs.

Comparing now between uncut and cut sampling areas; at both MH and CR the RQ values were reduced (from 0.24 to 0.21 and from 0.25 to 0.20, respectively) by removing the green matter, as might be expected with the removal of the photosynthetic oxygen source. These reductions are very small, and if they are reliable figures, they suggest a smaller drop in CO_2 than might be expected and possibly, therefore, a source of CO_2 other than surface respiration. The source of oxygen for this deeper in the peat is not obvious.

4.2.9 SHORT-TERM RESPONSE OF SURFACE FLUX TO WATER LEVEL AND TEMPERATURE CHANGES

In order to determine how quickly the peat cores responded to changes in environmental conditions, specifically to the water level imposed, gas fluxes from all cores were monitored daily before and after altering the water levels ready for stage III of the garden experiment. The final sample taken from cores with their water levels at the stage II height were collected on 11 September 1983. The water levels were then altered to those required for stage III and by

12 September they were all correct. Lids were replaced on the buckets and an initial (stage III) sample was taken. Thereafter samples of gas were removed at approximately 24-hour intervals until 15 September. Samples were withdrawn from the enclosed air in the bucket via the PVC sampling tube passing through the bung in the lid; samplers were not used for any of the samples, and bucket lids were left sealed in place. Water levels were measured on 10 September (stage II), checked on 12 and were next measured on 26 September. Fig. 4.50 shows the short-term changes in gas flux over the six days of the II→III changeover. The two parts of Fig. 4.50 each show the changes in flux of one component and compare that from uncut and cut pools, lawns and hummocks. The mean flux for each group of cores is shown. In addition to the spot gas fluxes, the mean flux for each of stages II and III is shown for comparison alongside, for control and experimental cores. In Fig. 4.50a only, the mean water level for each group as measured on 10 and 26 September is shown to the right of the gas flux plot. In addition the mean water levels for the entire stage II and stage III periods are shown on the far right, for each group.

On 10 September the air temperature in the garden was 15°C when the lids were put on the buckets. At sampling, on 11 September, the temperature was 11.5°C. Throughout the rest of the changeover period, to 15 September, the air temperature was 14.0 ±0.5°C at sampling (0900h). The maximum daily temperature range for the peat-air interface was about 7°C. The peat temperature varied by up to about

FIG. 4.51 Temperature changes during the changeover II→III period

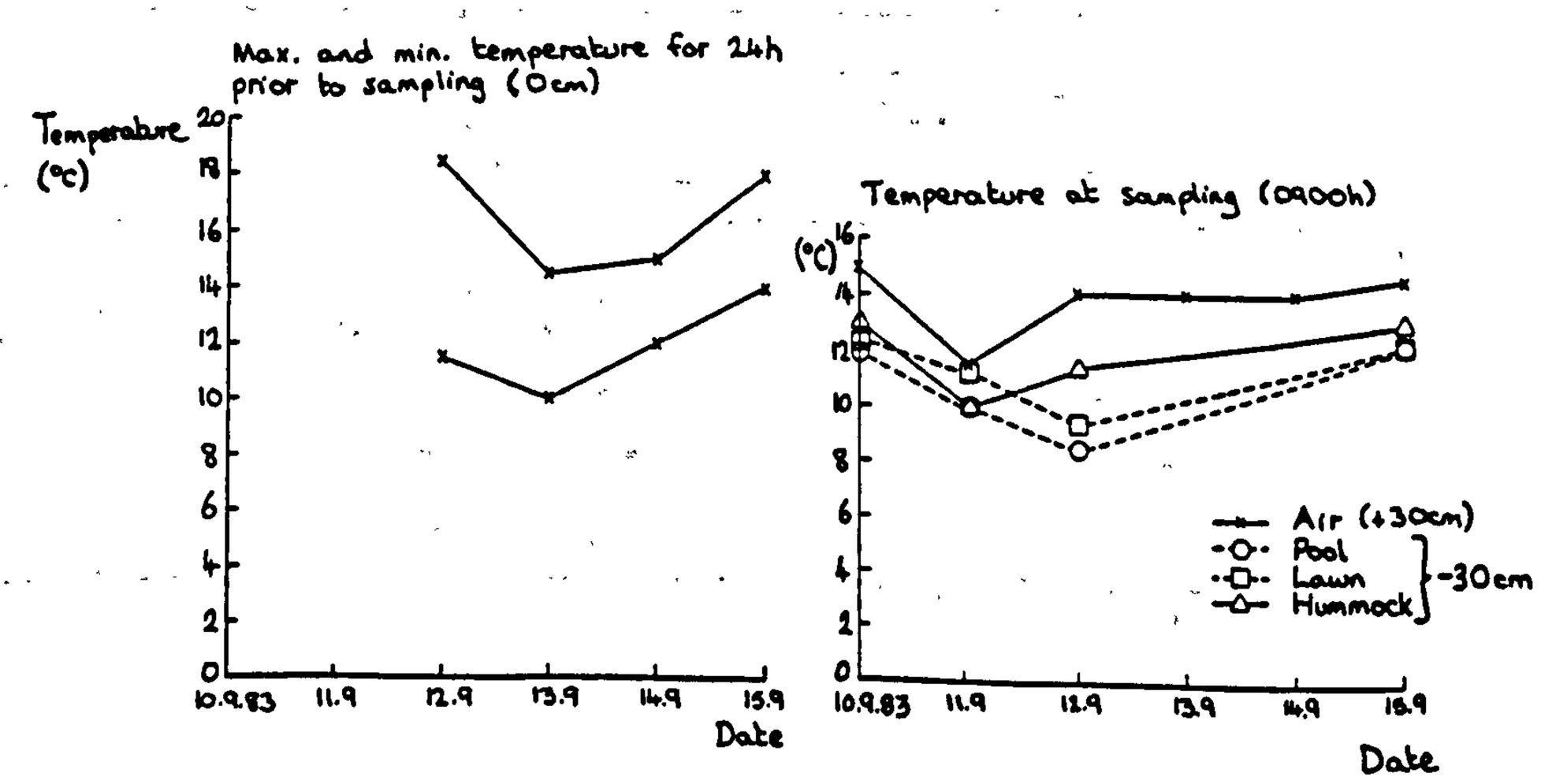
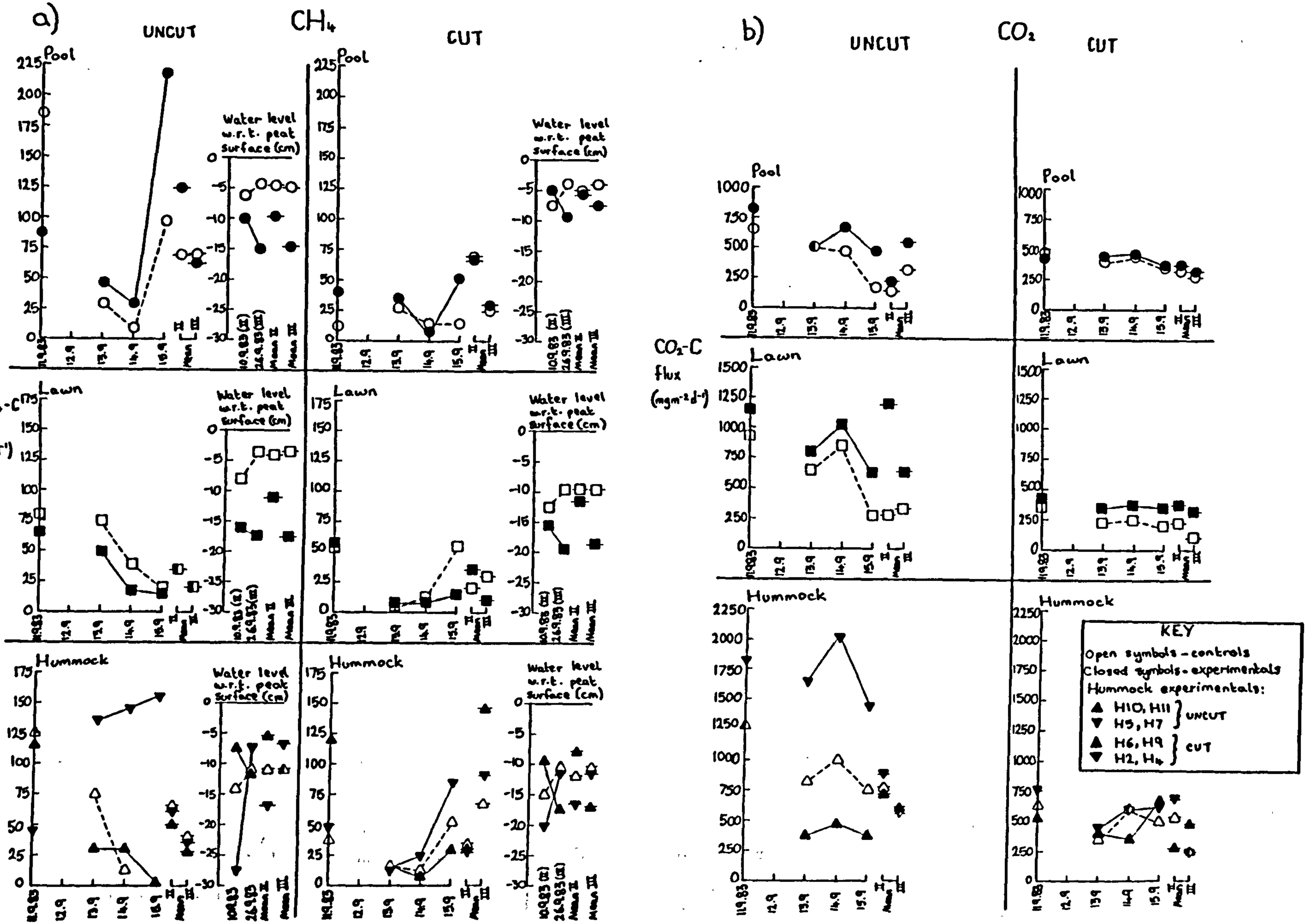


FIG. 4.50 Short-term changes in garden surface flux in response to water level changes



4°C (Fig. 4.51) over the whole changeover period. Despite no extreme temperature fluctuations, the response of the core gas fluxes did not consistently reflect the water level changes. Fluxes both increased and decreased, indicating that the changes were not simply a result of removing 20 ml of the gas at each sampling. It can be assumed that this was replaced within the sampling period.

In general, the short-term responses reinforced the pattern seen in the longer-term results, in that there was a larger difference between the fluxes from uncut core groups than between those of the cut cores. There were appreciable changes in gas flux from day to day, often showing a reversal in an upward or downward trend on successive days, suggesting a reasonably short response time of the cores to environmental change (though not obviously to water level and temperature). Notably, carbon dioxide fluxes showed such reversals more than those of methane, a feature presumably due to the fact that they were more affected by surface temperatures and respond immediately to changes. Methane flux is, to some degree, more dependent on conditions within the peat core, particularly those below the water level, so the changes in flux observed at the surface are likely to be more gradual, and fewer erratic changes in direction might be expected because of the integration effect. There was an interesting exception to this in the case of pools, where methane production might be expected to occur up to the surface water level and therefore to be affected more by surface conditions, than in lawn and hummock cores.

4.3 GAS CONCENTRATION PROFILES

4.3.1 INTRODUCTION

The location of the peat profile gas samplers at each Site, their position in the profile and their installation, have been described in Section 3.3.3, Deep Peat Gas Samplers. The first reliable samples were collected in December 1981, and the present section reports analyses carried out on data collected on each field visit (13 in total) from then until September 1983. A full complement of samples

for each visit was 15 from MH (three profiles) and 26 from CR (five profiles). The only sampler positioned at 2.5 m (CR, site 16) failed early on (bubbles appeared at the surface as it was being filled, and only a few cm^3 of gas could be withdrawn at sampling) and the results from it were unreliable.

The below-surface gas samples allowed measurement of component concentrations at fixed points down the peat profile. The v/v concentrations (vpm) arrived at from the gas chromatograms were converted to m/v concentrations (ppm) prior to any statistical analysis, using the appropriate conversion factors given in Table D.1, p.432.

Between October 1981 and June 1982 the samplers were inflated with air, but thereafter pure N_2 was used. Thus, gas samples collected between December 1981 and August 1982, inclusive, were from air-filled samplers, and subsequently they were from N_2-filled samplers. A paired t-test carried out between all the available matched-sample (by month and sampler) peat gas concentrations collected in 1982 and 1983 (April, May, June, August; n=164) and thus representing air-filled and N_2-filled sampler results, respectively, returned a significant result ($p<0.01$); so in all subsequent analyses the two sets of data were treated separately.

Sampling periods for peat profile samplers, that is the time between inflation at the end of one field visit and removal of the gas sample at the end of the following visit, varied between 31 days and 164 days. This was unavoidable, and to assess whether or not the peat gas sample contents were significantly affected, two samplers were placed at the base (-80 cm depth) of M1 in the garden in May 1983, and these were sampled repeatedly at intervals of between 2 days and 3 months. The monitoring ended in May 1984. The results indicated that the concentration of gases in the sample changed over the first 14 days after inflation, but between about 14 days and 3 months there was no further change. All the field profile sampling periods except those for April collections fell within this range. The April collections were made after 123 days and 164 days in 1982 and 1983, respectively. Analyses of variance were carried out with and without April data for MH, CR and MH & CR data together and the results for

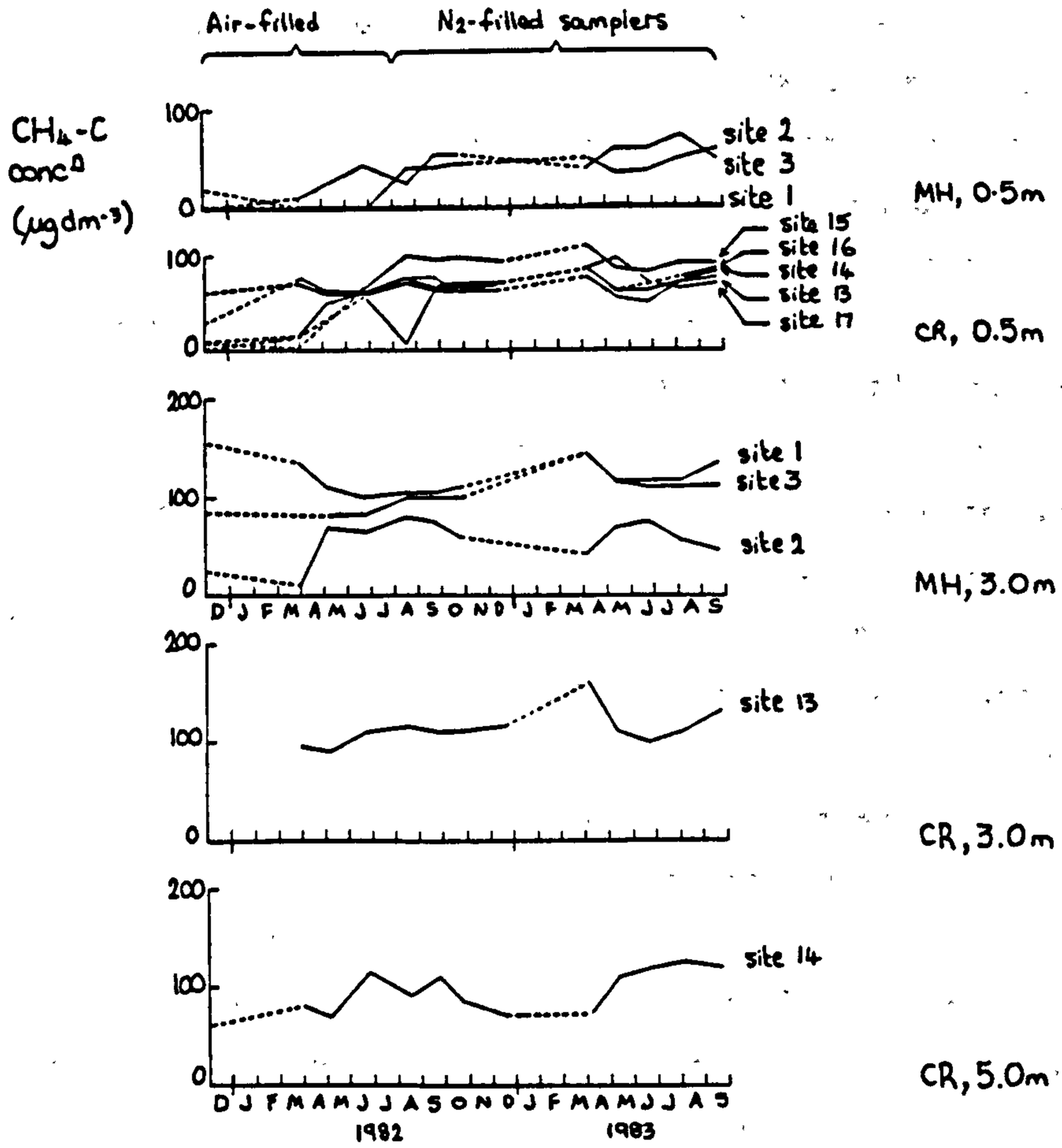
both methane and carbon dioxide were unaffected by its inclusion or exclusion, with one exception. Coom Rigg data from N_2-filled samplers gave a highly significant result for the seasonal (DATE) effect on CH_4-C concentration when April data were included, but at most depths the effect was non-significant when the April data were removed (Table 4.42, below). From this it was assumed that the prolonged sampling period over the winter did not affect the comparability of the data and the following account refers to the results from analyses which included April data unless stated otherwise.

In May 1982 peat profile gas samples were collected at the beginning of the visit, after a sampling period of 33 days, after which the samplers were re-inflated (with air) and sampled again at the end of the visit, 3 days later. At MH and CR the concentration of CH_4-C in the 3-day samples was between 0.5x and 0.66x that in the 33-day samples. The 3-day samples from site 3 showed a higher proportional concentration of methane compared with the corresponding 33-day samples, the deeper the sampler; but such a trend was not evident at sites 1 and 2. At sites 14 and 15 there was an increase in the proportion with depth; but not at sites 13, 16 or 17. In all, 39 samples were collected at the end of the 3-day sampling period (out of a possible total of 41), compared with only 29 after 33 days. The reduced number of samples were collected because there remained only a small volume ($\simeq$ 5 cm^3) of gas in the other samplers. This may have been attributable to the longer sampling period, but is more likely to be the result of leakage through the taps, under pressure. After removal of the 33-day sample, and thereafter, 'screw-gate' clamps (Hofmann clips) were placed just behind the 3-way tap on the tubing connecting the sampler to the surface.

There was much variation in the relative concentrations of carbon dioxide in the 3-day and 33-day samples. In most cases the 3-day samples contained much greater concentrations of CO_2-C than did the 33-day samples. In those cases where the 33-day sample contained a higher CO_2-C concentration than the 3-day sample, the difference was only small. There was no apparent relationship with depth.

The samples collected after three days have been omitted from the analyses reported below.

FIG. 4.52 Time-course of methane concentrations in selected individual profile samplers



There was no evidence that a sampler drained a volume of peat of its CH_4, since the sample concentration did not decrease on successive trips (Fig. 4.52). The same was true for CO_2.

4.3.2 CORRESPONDENCE BETWEEN REPLICATE SAMPLES

Triplicate samples were provided by the three sites at MH (samplers at 0.2 m, 0.5 m, 1.0 m, 2.0 m and 3.0 m depth). Because there is some reason for expecting that the steady-state concentration profiles for different total depths of peat will be different (Clymo, 1984, Fig. 15), only sites 13 and 15 at CR were considered to be true replicates, despite samplers being positioned at each of the five

TABLE 4.41 Summary of methane and carbon dioxide concentration profile analyses of variance results.

SITE, DEPTH, SITE.DEPTH treatments

CH_4

Depth class (m)	Inflation gas	April Data	Moor House SITE	Moor House DEPTH	Moor House SITE.DEPTH	Coom Rigg SITE	Coom Rigg DEPTH	Coom Rigg SITE.DEPTH
0.2-0.5	air	with	**	**	ns	ns	***	ns
0.2-0.5	air	without	*	*	ns	ns	***	ns
0.2-0.5	N_2	with	***	***	***	ns	***	***
0.2-0.5	N_2	without	***	***	***	ns	***	***
1.0-3.0	air	with	***	***	ns			
1.0-3.0	air	without	**	***	ns			
1.0-3.0	N_2	with	***	***	***			
1.0-3.0	N_2	without	***	***	***			
2.0-4.0	air	with				ns	ns	ns
2.0-4.0	air	without				ns	ns	ns
2.0-4.0	N_2	with				ns	**	ns
2.0-4.0	N_2	without				ns	**	ns
2.0-3.0	air	with	***	*	ns			
2.0-3.0	air	without	*	*	ns			
2.0-3.0	N_2	with	***	ns	***			
2.0-3.0	N_2	without	***	ns	***			

CO_2

Depth class (m)	Inflation gas	April Data	Moor House SITE	Moor House DEPTH	Moor House SITE.DEPTH	Coom Rigg SITE	Coom Rigg DEPTH	Coom Rigg SITE.DEPTH
0.2-0.5	air	with	**	ns	ns	ns	***	ns
0.2-0.5	air	without	*	ns	ns	ns	***	ns
0.2-0.5	N_2	with	***	***	***	ns	*	ns
0.2-0.5	N_2	without	***	***	**	ns	*	ns
1.0-3.0	air	with	**	ns	ns			
1.0-3.0	air	without	ns	ns	ns			
1.0-3.0	N_2	with	**	***	***			
1.0-3.0	N_2	without	**	**	***			
2.0-4.0	air	with				ns	ns	ns
2.0-4.0	air	without				ns	ns	ns
2.0-4.0	N_2	with				ns	ns	ns
2.0-4.0	N_2	without				ns	ns	ns
2.0-3.0	air	with	ns	ns	ns			
2.0-3.0	air	without	ns	ns	ns			
2.0-3.0	N_2	with	***	ns	***			
2.0-3.0	N_2	without	**	ns	**			

sites at 0.2 m, 0.5 m and 1.0 m. Three samples were collected at 2.0 m and 4.0 m, and single samples from 2.5 m, 3.0 m and 5.0 m.

Results from analyses of variance between 'replicate' (*sens. lat.*) site and depth data sets were used to assess the absolute extent of correspondence, so providing a test of the theory (Table 4.41). They showed that, at CR, 'replicate' sample CH_4-C and CO_2-C concentrations did not differ significantly ($p>0.05$). At MH there was no such correspondence at any depth. All 'replicate' CH_4 samples were significantly different; $p<0.001$ for those where N_2 had been used for inflation. Results were similar for MH CO_2-C concentrations, but the significance levels were, on the whole, slightly lower.

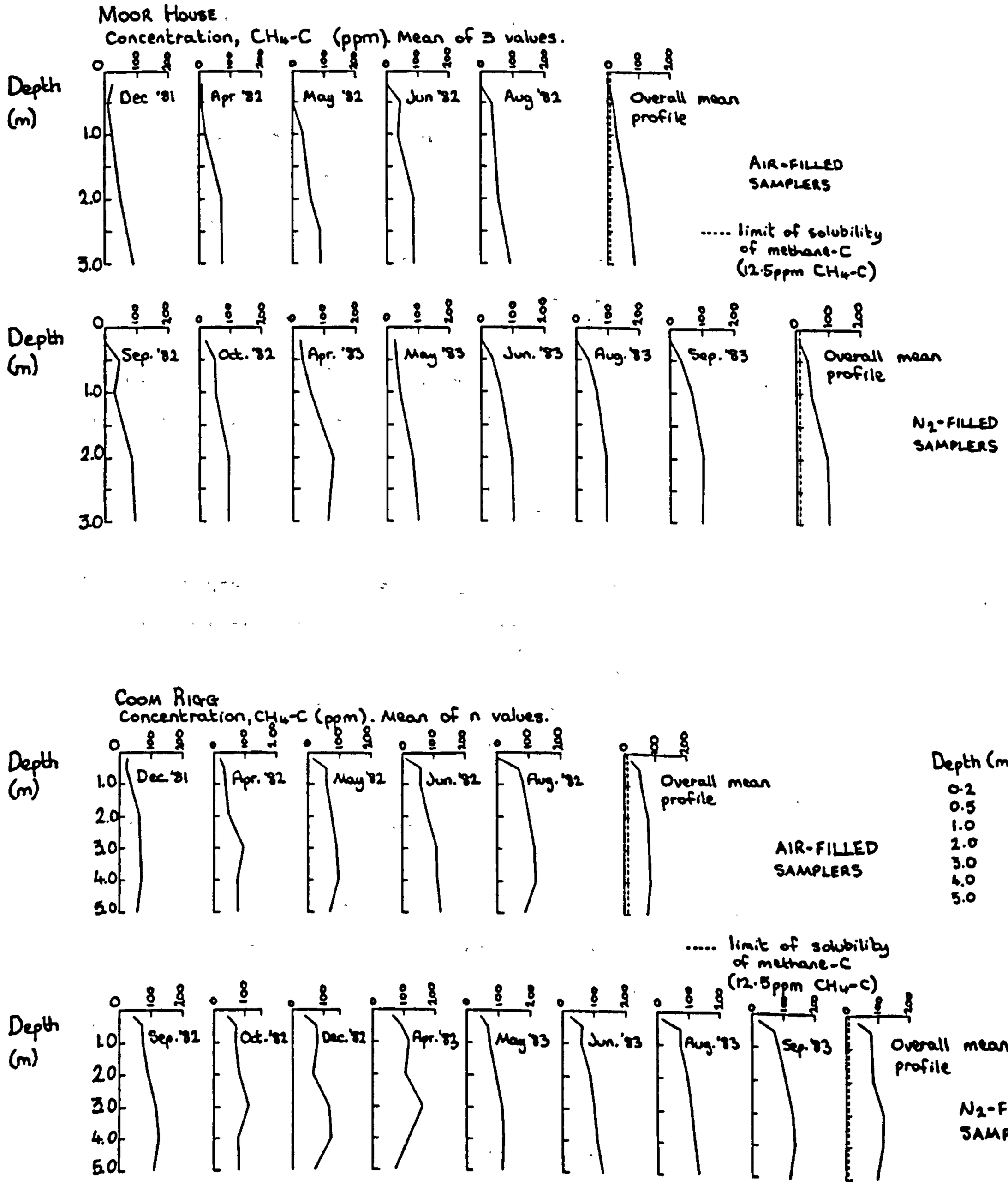
These results - the lack of correspondence between theoretically-true replicates at MH and a close correspondence between theoretical non-replicates at CR - do not necessarily invalidate the theory. The calculated concentration profiles in Clymo (1984) are based on a number of assumptions about a homogeneous, 'ideal' peat mass. Clymo acknowledged that the calculations were "rather artificially constrained". Therefore we should not be hasty in rejecting the general theory on the basis of minor discrepancies of detail. It is clear from Clymo's Figure 15 that the difference in theoretical steady-state gas concentrations between two profiles of different total depth increases with depth, but that between the deeper (total) profiles the difference is less than between shallower ones. Hence we should expect less difference between the 4 m and 5 m profiles at CR than between 3 m and 3.5 m profiles at MH. Furthermore, the nature of the peat making up the shallow and deep profiles at CR is more variable than that at MH and this effect may well swamp any smaller effect of total peat depth. Peat heterogeneity, and the complex chemistry which this supports, may explain the lack of correspondence between the MH profiles.

For the analysis of the gas profile data, MH and CR data were treated separately. Individual site data were clumped together where appropriate, but the inherent between-site differences at MH must be borne in mind when considering the results of such analyses.

Correspondence Between Replicate Samples

Corresponding depth samples at CR have been considered as replicates where appropriate.

FIG. 4.53 Methane concentration profiles at Moor House and Coom Rigg, December 1981 - September 1983



4.3.3 METHANE

EFFECT OF DEPTH

MH and CR data were analysed separately, and compared. The CH_4-C concentration profiles are shown in Fig. 4.53 (note the different vertical scales), and the results of analyses of variance for DEPTH and DEPTH.DATE effects are shown in Table 4.42.

It is clear from the Figs. that, in general, the concentration of CH_4-C increased considerably with depth and that the increase was significant (Table 4.42). The profiles are not linear, but show the fastest change in concentration over the top 50 cm. Below this the concentration continues to increase, but more slowly. At least 75% of the maximum concentration is reached at 2 m depth.

Profile shapes are similar, but samples from N_2-filled samplers gave higher CH_4-C concentrations (by 10-50 ppm) than those from air-filled ones. Possible reasons for this are discussed in Chapter 5.

All CR samples contained higher concentrations of CH_4-C than did the corresponding MH samples.

One other general feature of the profiles may be worth noting. Several showed a decrease in CH_4-C concentration at the deepest point, and in three cases also between 3.0 m and 4.0 m.

Considering first the data from air-filled samplers, the overall mean increase in CH_4-C concentration over the 3 m MH profile was from 5 ppm to 85 ppm, compared with from 20 ppm to 80 ppm over the top 3 m at CR. At CR there was insignificant change in concentration below this. Thus the relative increase in concentration was, on average, greater at MH than at CR despite the shallower peat. This was so in all recorded months while air was used, except December 1981 and August 1982, and was attributable to the very low concentrations of CH_4-C at 0.2 m ($\leq$10 ppm in all cases except December 1981) compared with those at CR ($\leq$10 ppm on only two occasions). The CH_4-C concentrations at 3.0 m were between 75 ppm (April 1982) and 95 ppm (August 1982) at MH, and between 70 ppm (December 1981) and 115 ppm

TABLE 4.42 Summary of methane concentration profile analyses of variance results.

DEPTH, DATE, DEPTH.DATE treatments

Depth class (m)	Inflation gas	April data	Moor House DEPTH	Moor House DATE	Moor House DEPTH,DATE	Coom Rigg DEPTH	Coom Rigg DATE	Coom Rigg DEPTH,DATE
All	air	with	***	ns	ns	***	***	ns
0,2-0,2	air	with		ns			ns	
0,2-0,5	air	with	ns	ns	ns	**	ns	ns
0,2-1,0	air	with	**	ns	ns	***	*	ns
0,2-2,0	air	with	***	ns	ns	***	**	ns
0,5-5,0	air	with	***	ns	ns	***	***	ns
1,0-5,0	air	with	**	ns	ns	***	***	ns
2,0-5,0	air	with	ns	ns	ns	***	***	ns
All	air	without	***	ns	ns	***	***	ns
0,2-0,2	air	without		ns			ns	
0,2-0,5	air	without	ns	ns	ns	***	ns	*
0,2-1,0	air	without	**	ns	ns	***	**	*
0,2-2,0	air	without	***	ns	ns	***	***	ns
0,5-5,0	air	without	***	ns	ns	***	***	ns
1,0-5,0	air	without	**	ns	ns	***	***	ns
2,0-5,0	air	without	ns	ns	ns	***	***	ns
All	N_2	with	***	ns	ns	***	***	**
0,2-0,2	N_2	with		*			***	
0,2-0,5	N_2	with	***	ns	ns	***	***	*
0,2-1,0	N_2	with	***	ns	ns	***	***	**
0,2-2,0	N_2	with	***	ns	ns	***	***	**
0,5-5,0	N_2	with	***	ns	ns	***	***	ns
1,0-5,0	N_2	with	***	ns	ns	***	**	ns
2,0-5,0	N_2	with	ns	ns	ns	***	ns	ns
All	N_2	without	***	ns	ns	***	ns	*
0,2-0,2	N_2	without		*			**	
0,2-0,5	N_2	without	***	ns	ns	***	*	*
0,2-1,0	N_2	without	***	ns	ns	***	*	*
0,2-2,0	N_2	without	***	ns	ns	***	ns	***
0,5-5,0	N_2	without	***	ns	ns	***	*	ns
1,0-5,0	N_2	without	***	ns	ns	***	**	ns
2,0-5,0	N_2	without	ns	ns	ns	***	ns	ns

(August 1982) at CR. At 5.0 m at CR the concentrations were between 60 ppm (December 1981) and 120 ppm (June 1982).

Over the top 1 m of peat both MH and CR showed significant changes (increases) in CH_4-C concentration ($p<0.01$ at MH and $p<0.001$ at CR). Towards the base of the peat at MH, specifically between

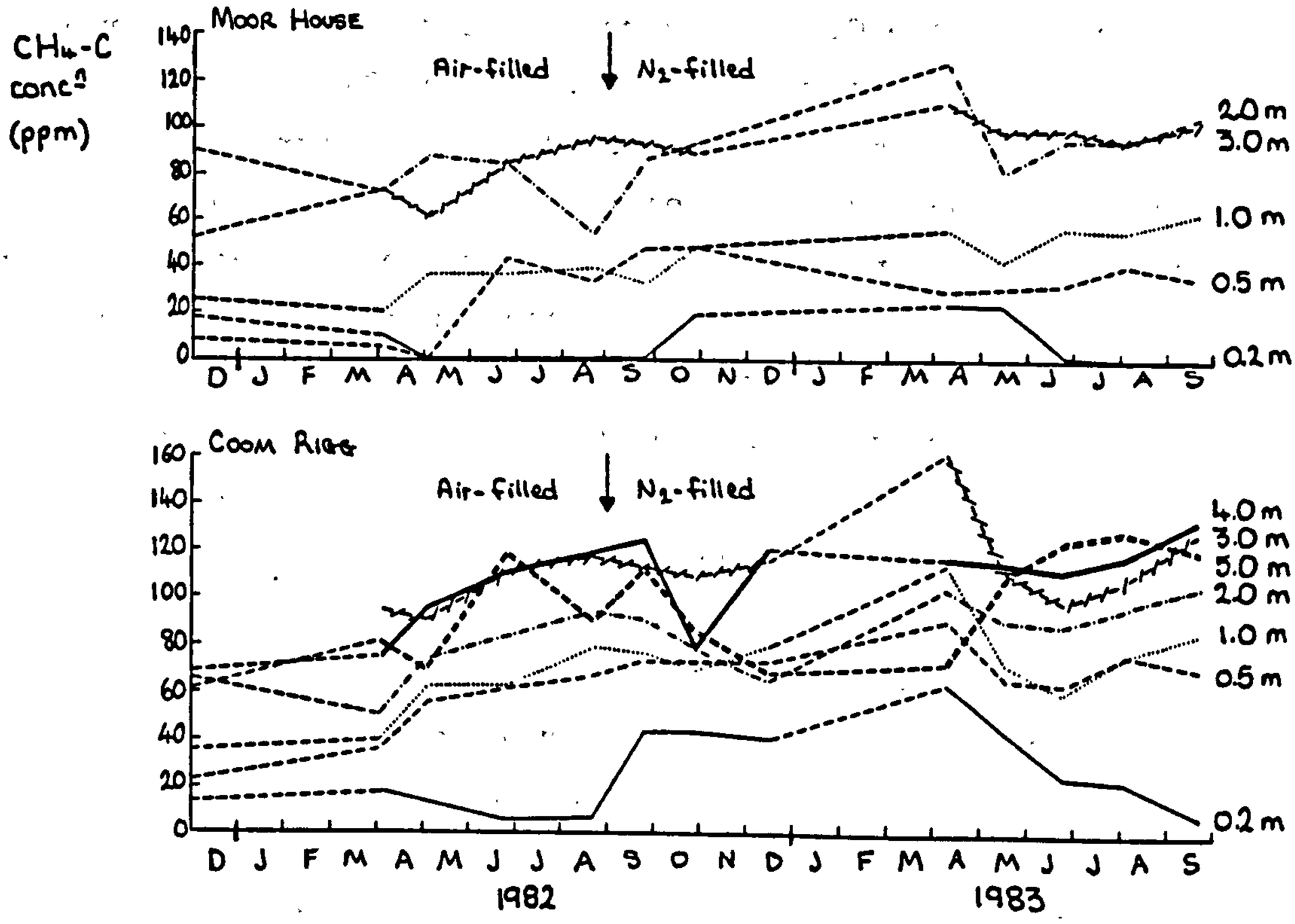
2.0 m and 3.0 m, there was no significant change in CH_4-C concentration, but between 2.0 m and the deepest sample of the CR profiles the concentration did increase significantly ($p<0.001$). This probably reflects the exponential form of the increase in concentration, such that a one metre interval at a depth of 2.0 m to 3.0 m is insufficient to register a significant increase in concentration, whereas a three metre interval beginning at the same depth does show such an increase, albeit small in absolute terms.

Despite apparent differences in the slope of the MH profiles at comparable depths at different times of the year, no analysis of variance returned a significant result for the DEPTH.DATE treatment. However, the same tendency for a rise in the rate of increase of CH_4-C concentration over the 0.2-0.5 m interval was apparent, both at MH and CR, and CR data returned a number of significant results from analyses of variance (DEPTH.DATE treatment) carried out on data from N_2-filled samplers for depth classes covering the top portion of the profile, down to 2.0 m (Table 4.42).

SEASONAL CHANGE

Fig. 4.54 shows the seasonal variation in CH_4-C concentration at each depth for MH and CR. The left-hand portion of each plot represents data from air-filled samplers. At MH the changes in CH_4-C concentration were large and inconsistent, such that an analysis of variance returned a non-significant result for all depths (Table 4.42). At CR, the concentration of CH_4-C tended to increase between April and August 1982, at depths between 0.5 m and 4.0 m. Results from 5.0 m were surprising in that they showed large, apparently erratic, fluctuations in concentration. The seasonal increase was significant ($p<0.05$) below 50 cm but not above, apparently, when air was used. Down to 3 m there was an increase in the seasonal range of concentration with depth, from 37 ppm at 0.2 m to 50 ppm at 3 m. This was accompanied by a tendency for the peak concentration to occur earlier in the year at successive depths. Below this the annual concentration range was reduced, and at 4 m the seasonal changes were almost exactly out of phase with those at 2 m.

FIG. 4.54 Seasonal changes in methane concentration at sampler depths at Moor House and Coom Rigg, December 1981 - September 1983



The results from the N_2-filled samplers are somewhat less erratic. The range of concentrations at any given depth at CR was larger than that at MH, by up to three times. Analyses of variance carried out to determine the significance of the seasonal changes (1983; N_2-filled) returned highly significant ($p<0.01$) results for all depths at CR, but were non-significant for MH except at 0.2 m ($p<0.05$).

The CR N_2-filled sampler results showed a tendency for the minimum CH_4-C concentration to occur earlier in the season deeper down (cf September at 0.2 m and June at 4.0 m) and, with the exception of the 3 m results, a tendency for the minimum to become less pronounced with depth. The 5 m seasonal changes showed a similar out-of-phase shift relative to those at 0.2 m, as was seen in the previous year, although the general shape of all the curves was markedly different between the two years.

4.3.4 CARBON DIOXIDE

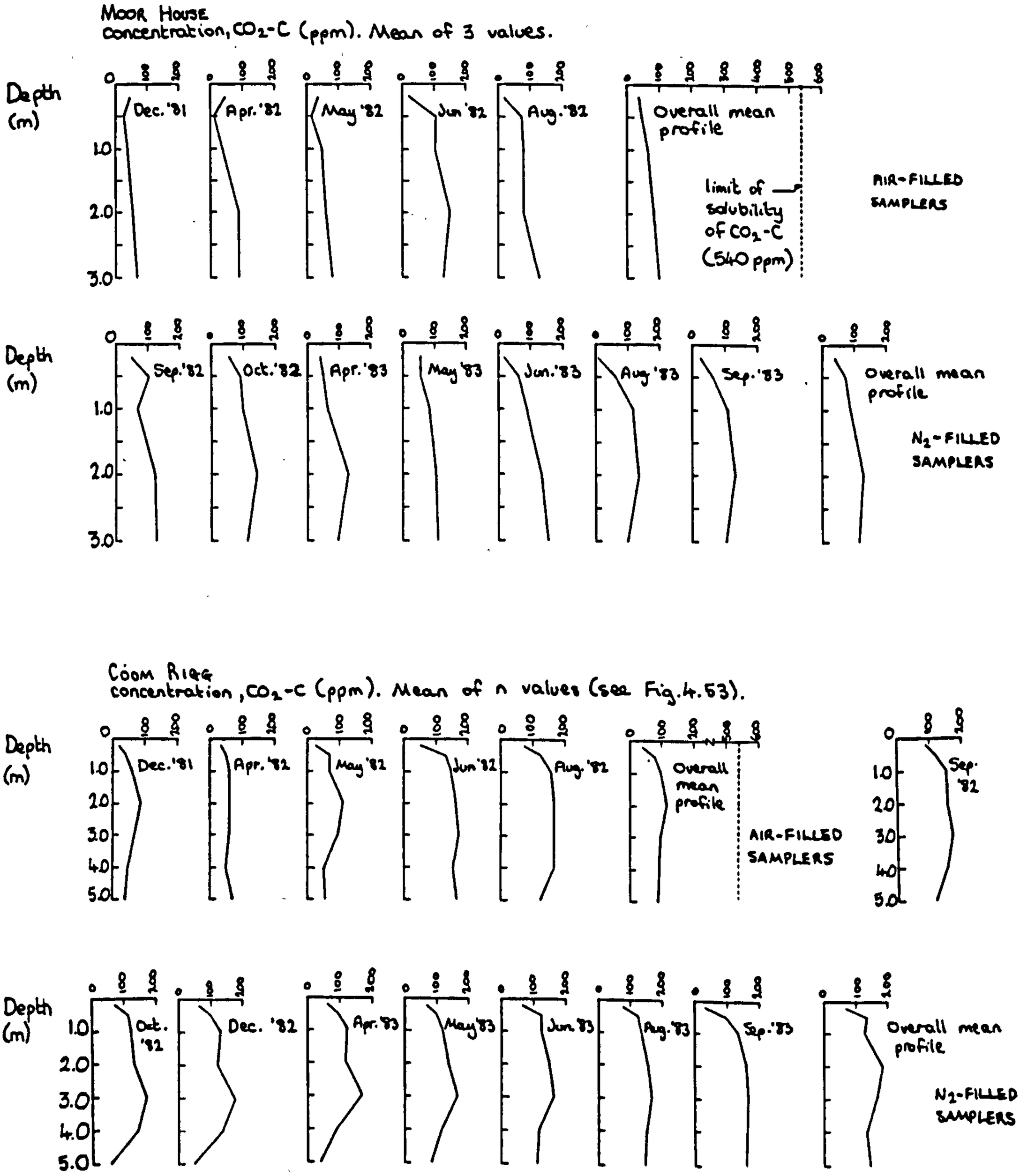
EFFECT OF DEPTH

Fig. 4.55 shows the CO_2-C concentration profiles measured on each field visit between December 1981 and September 1983 for MH and CR, respectively. The order of magnitude of the concentrations was the same as that of CH_4-C, but in nearly all cases the precise CO_2-C concentration was greater. Furthermore, the difference was greater in samples obtained from N_2-filled samplers than from air-filled ones.

As for CH_4-C, there was an increase in CO_2-C concentration with depth, the fastest increase occurring in the top 50 cm of peat, below which the rate of increase slowed, and in some instances began to decrease one or two metres above the base of the peat. At MH the overall mean profile from the air-filled sampler data shows an increase from 35 ppm CO_2-C at 0.2 m to a maximum of 100 ppm at the base. This compares with an increase from 40 ppm CO_2-C at 0.2 m to a maximum of 130 ppm at 2.0 m and a slight drop to 115 ppm at 3.0 m based on N_2-filled sampler data. At CR the air-filled samplers showed an increase in concentration from 60 ppm CO_2-C at 0.2 m, increasing to a maximum of 180 ppm at 3.0 m and then falling to 50 ppm in the 5.0 m sample. N_2-filled sampler concentrations increased from 70 ppm CO_2-C at 0.2 m to 185 ppm at 2.0 m, below which the concentration fell to around 140 ppm. Thus there was a tendency, particularly at CR, for the maximum CO_2-C concentration to occur closer to the surface (at 2.0 to 3.0 m) than that of CH_4-C (3.0 and 4.0 m).

Table 4.43 (air-filled samplers) indicates highly significant changes in CO_2-C concentrations with depth for all depth classes down to, and including, 2.0 m ($p<0.001$) at CR, whereas corresponding results for MH were nearly all non-significant or, at best, they showed a significant difference at only the $p<0.05$ level. The two Sites also differed in their basal profiles: at CR the CO_2-C concentrations continued to change throughout the profile, though they did not always continue to increase towards the base, and the overall mean profile indicated a small decrease. At MH there was no significant change in CO_2-C concentration below 1 m.

FIG. 4.55 Carbon dioxide concentration profiles at Moor House and Coom Rigg, December 1981 - September 1983



When the results from analyses of variance for DEPTH effects on CO_2-C concentration (N_2-filled samplers) are compared, the situation is reversed; the depth effect was highly significant for all depth

TABLE 4.43 Summary of carbon dioxide concentration profile analyses of variance results.

DEPTH, DATE, DEPTH.DATE treatments

Depth class (m)	Inflation gas	April data	Moor House DEPTH	Moor House DATE	Moor House DEPTH.DATE	Coom Rigg DEPTH	Coom Rigg DATE	Coom Rigg DEPTH.DATE
All	air	with	**	*	ns	***	***	ns
0,2-0,2	air	with		ns			**	
0,2-0,5	air	with	ns	ns	ns	**	*	ns
0,2-1,0	air	with	ns	ns	ns	***	***	ns
0,2-2,0	air	with	*	*	ns	***	***	ns
0,5-5,0	air	with	*	**	ns	**	***	ns
1,0-5,0	air	with	ns	*	ns	*	***	ns
2,0-5,0	air	with	ns	ns	ns	**	***	ns
All	air	without	**	**	ns	***	***	ns
0,2-0,2	air	without		ns			**	
0,2-0,5	air	without	ns	ns	ns	***	***	ns
0,2-1,0	air	without	ns	ns	ns	***	***	ns
0,2-2,0	air	without	ns	*	ns	***	***	ns
0;5-5,0	air	without	ns	**	ns	**	***	ns
1,0-5,0	air	without	ns	*	ns	**	***	ns
2,0-5,0	air	without	ns	ns	ns	**	***	ns
All	N_2	with	***	ns	ns	*	ns	ns
0,2-0,2	N_2	with		**			*	
0,2-0,5	N_2	with	**	ns	ns	*	ns	ns
0,2-1,0	N_2	with	***	ns	ns	**	ns	ns
0,2-2,0	N_2	with	***	ns	ns	*	ns	ns
0,5-5,0	N_2	with	***	ns	ns	ns	ns	ns
1,0-5,0	N_2	with				ns	ns	ns
2,0-5,0	N_2	with	ns	ns	ns	ns	ns	ns
All	N_2	without	***	ns	ns	ns	ns	ns
0,2-0,2	N_2	without		*			*	
0,2-0,5	N_2	without	**	ns	ns	*	ns	ns
0,2-1,0	N_2	without	***	ns	ns	*	ns	ns
0,2-2,0	N_2	without	***	ns	ns	*	ns	ns
0,5-5,0	N_2	without	***	ns	ns	ns	ns	ns
1,0-5,0	N_2	without	*	ns	ns	ns	ns	ns
2,0-5,0	N_2	without	ns	ns	ns	ns	ns	ns

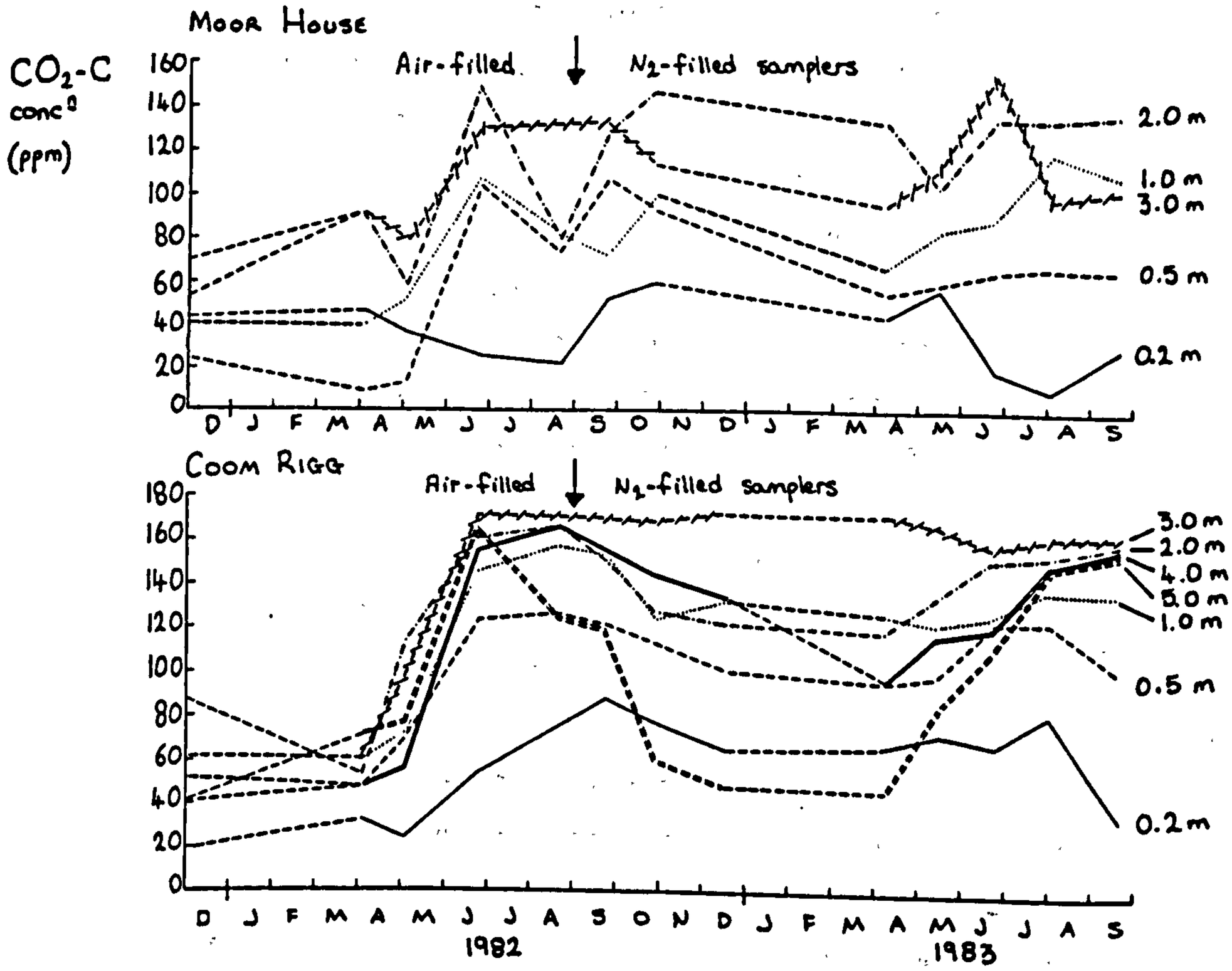
classes at MH, but its significance was much reduced at CR. It is not obvious from the Figures why this should be so, except that there was a more marked decrease in CO_2-C concentration below the depth of the maximum concentration at CR than at MH, although more than half the MH profiles also showed an absolute decrease in concentration below the

maximum, and all showed at least a slackening in the rate of increase. The microbiology may explain the difference. The proportion of CO_2 and CH_4 produced depends on various circumstances (Appendix M).

SEASONAL CHANGE

The changes in mean CO_2-C concentration recorded between December 1981 and September 1983 at each sampler depth are plotted in Fig. 4.56. The sequence and form of the traces at each depth are reasonably consistent, in both cases showing a general increase in CO_2-C concentrations beginning in April, peaking 2-3 months later and then falling off again to August or September. In a number of cases, especially at CR, there was a second increase in the autumn, though

FIG. 4.56 Seasonal changes in carbon dioxide concentration at sampler depths at Moor House and Coom Rigg, December 1981 - September 1983



this was less apparent in 1983 than 1982. Differences in the absolute concentrations at any given time between depths was smaller deeper down. There was a gradual shift in the seasonal changes as the depth increased, tending towards rather imperfect inversions, which resulted in the highest mean concentrations of CO_2-C being found at the intermediate depths of about 2-3 m, a point which was noted above, from the seasonal CO_2-C concentration profiles.

In absolute terms, the concentrations of CO_2-C were 20 ppm higher, or more, at a given depth at CR than at MH.

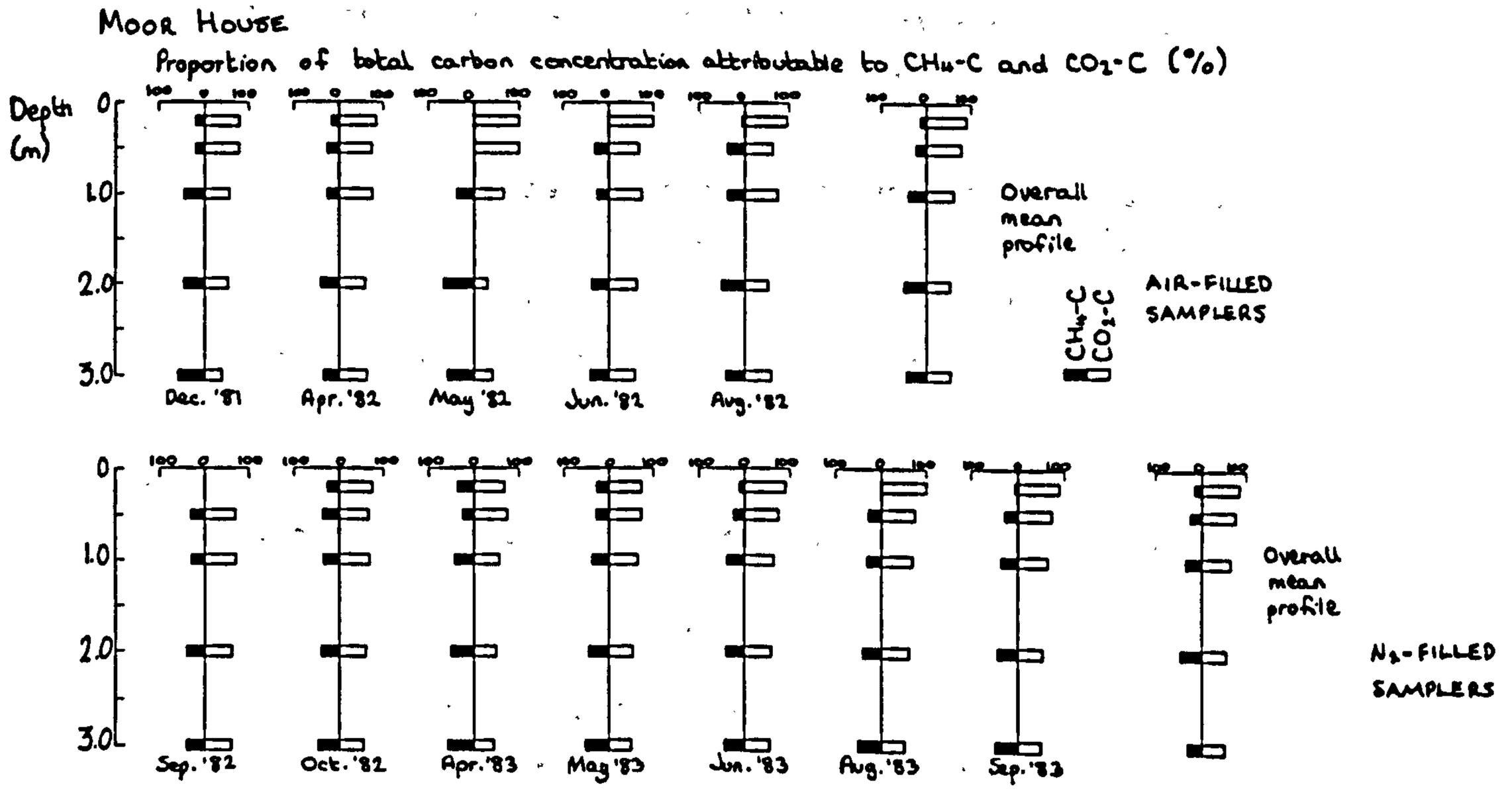
An effect of introducing air into the system is apparent from Fig. 4.56 from a comparison of the 1982 (air-filled) and 1983 (N_2-filled) results. Maximum CO_2-C concentration was achieved much more rapidly, in seasonal terms, but was not always higher, in those samplers filled with air.

4.3.5 PROPORTIONAL METHANE AND CARBON DIOXIDE CONCENTRATION PROFILES

Fig. 4.57 shows the relative concentrations of CH_4-C and CO_2-C at each depth recorded for all field visits between December 1981 and September 1983 at MH and CR, respectively. Plotted values represent the proportion (%, w/w) of total carbon as CH_4-C and CO_2-C, assuming no other contributory species.

It is clear that more carbon was present as carbon dioxide, overall, than as methane, but the methane proportion increased with depth. The relative concentration of CH_4-C increased rapidly from between 10% (MH) and 25% (CR) (air-filled) and 15% (MH) and 30% (CR) (N_2-filled) at 0.2 m, to between 20% (MH) to 40% (CR) and 25% (MH) to 40% (CR) (N_2) at 0.5 m, and then to between 48% (MH) to 50% (CR) (air-filled) and 48% (MH) to 55% (CR) at 2.0-5.0 m (N_2-filled). The roughly maximum CH_4-C proportion was reached at about 2.0 m, below which there was little change. The proportions varied slightly with season. A higher proportion of methane was present at colder times of the year near the surface, the maximum mean proportion at 0.2 m from air-filled samplers was 20% (MH) to 35% (CR) in December 1981. This decreased gradually over the 1982 season to 0% at MH (in May and June) and 8% at CR (in June and August). Corresponding figures for the

FIG. 4.57 Relative methane and carbon dioxide concentration profiles at Moor House and Coom Rigg, December 1981 - September 1983



N_2-filled samplers were 34% and 48% at MH and CR, respectively, in April, and <1% at MH and 13% at CR in August 1983. Thus, in general, when N_2 had been used to inflate the sampler, a slightly higher proportion of CH_4-C was recorded than when air had been used.

Four mean values from MH data showed a proportion of CH_4-C greater than 50%; three of these were recorded at 3.0 m and one at 2.0 m, and all were for the period between December and May, inclusive. The maximum mean proportion of CH_4-C was 59%, at 3.0 m in December 1981. Of the mean values at CR, eleven showed more than 50% of the total carbon present as CH_4-C, and all these records were in the period between October and May, inclusive. Of the eleven, all except one were for depths of 4.0 m or 5.0 m, the eleventh was calculated for 3.0 m. The maximum mean CH_4-C proportion was 63%, in May 1982 at 4.0 m.

At MH the proportion of CH_4-C in the 0.2 m and 0.5 m samplers was between 10% and 20% less (absolutely) than at corresponding depths at CR. Below this, to 3.0 m, there was no significant difference between the overall mean proportions at the two Sites. Furthermore, both MH and CR results indicated that the proportion of CH_4-C stabilised at about 2 m, irrespective of total peat depth. Both Sites showed the same trend of a decrease in the proportion of CH_4-C at 0.2 m with an increase in air temperature.

4.3.6 ANALYSIS OF FACTORS ASSOCIATED WITH GAS CONCENTRATIONS

It may be helpful to refer to Section 4.4, below, which describes the pH, redox potential and sulphide concentration characteristics of the field peat.

In an attempt to determine which measured attributes of the peat system were most closely associated with CH_4-C and CO_2-C concentrations, correlation coefficients were calculated between each of twelve variables and the concentration of CH_4-C and CO_2-C, in turn. The chosen variables represented chemical factors and temperature, and are listed in Table 4.44. The value of the pS variable was the mean of all available records falling within the 20 cm vertical interval of the peat profile corresponding to that of the sampler, plus any

TABLE 4.44 Variables used in correlation and regression analyses of CH_4-C and CO_2-C concentrations at Moor House and Coom Rigg.

Label	Description
CH_4, CO_2	CH_4-C or CO_2-C concentration (ppm) (dependent)
pS	pS (-log [total sulphide], mol dm^{-3}) (units).
E_h	E_h (mV)
pH	pH (units)
Air	Air temperature (+1.5 m) at time of record (study data) (°C)
MMAX	Met. Off. mean monthly maximum air temperature (°C)
MMIN	Met. Off. mean monthly minimum air temperature (°C)
MMEAN	Met. Off. mean monthly temperature (°C)
MHREC	Predicted peat temperature at depth and time of record. calculated from sine wave equation based on MH data collected during study: $T_{(z,t)} = 4.8 + 16.0\ e^{-z/40.0}\ Sin((2\pi/365.0)-z/40.0)$ (°C)
METREC	As MHREC, but calculated from sine wave equation based on 1981 Met. Off. data: $T_{(z,t)} = 4.9 + 7.5\ e^{-z/80.0}\ Sin((2\pi/365.0)-z/80.0)$ (°C)
MHLAST	As MHREC, for period since previous field visit (°C)
METLAST	As METREC, for period since previous field visit (°C)
MEDLAST	Median peat-air interface temperature (+5 cm) since previous field visit (°C)

representing depths 5 cm above or below this range. It should be borne in mind that peat sulphide, redox potential and pH were not measured immediately adjacent to the peat gas samplers (Table 4.54, below). Analyses were carried out on different sub-sets of data, representing samples collected from air-filled and N_2-filled samplers, from different depth classes, and both with and without April data. Data from individual sampling areas were analysed separately for comparison between sites at MH and CR, respectively, though any results from such analyses must be treated with caution since the correlation coefficients were calculated using the same values for the independent variables; only the dependent variables changed. More reliable indications of the most important factors were obtained when data from all the sites at MH and CR, respectively, were grouped together. The entire set of MH & CR data was also analysed as one. The size of each data set subjected to correlation analysis is shown in Table 4.45; only those with $n \geq 5$ were used.

Next, a series of regression analyses were carried out on similar sub-sets of data to determine i) the significance of any (linear)

TABLE 4.45 Data sets used in correlation and regression analyses of CH_4-C and CO_2-C concentrations at Moor House and Coom Rigg. Values represent size of data set, n. Values for CH_4-C analyses are given; where those for CO_2-C differed they are shown as a superscript.

Depth class (m)	Inflation gas	April data	MEDLAST	Sites 1	2	3	MH	13	14	15	16	17	CR	MH&CR
All	Air	+	-	5	6	5	16	10^{11}	6^{7}	11	9	8	44^{46}	60^{62}
	Air	-	-				6	5^{6}		6			21^{22}	27^{28}
	N_2	+	-	25	32	33	90	34	27	23	24	25	133	223
0,2-0,5	Air	+	-				6			5			18	24
	N_2	+	-	6	14	14	34	14	13	8	7	14	56	90
2,0,4,0	Air	+	-						5					
	N_2	+	-					8	9	8				
All	N_2	+	+	12	14	14	40	10	9	7	8	7	41	31

relationship between CH_4-C and CO_2-C concentrations and the independent variables in Table 4.44, and what proportion of the variation in concentration was thus accounted for (r^2); and ii) the significance and variation accounted for in different data sets by comparable 'model' multiple linear regressions involving all chemical variables, air temperature and the 'best' temperature variable (see below for details).

METHANE

A summary of the correlation coefficients for the association between CH_4-C concentrations and the variables in Table 4.44 for the MH, CR and MH & CR data sets is given in Table 4.46. A summary of the main results discussed in this section are shown in Table 4.47, to help in following the rather detailed account below. The full table of significant individual r^2 values for the regression of CH_4-C concentration on each in turn is given in Appendix Na.

The correlation coefficients indicated that, over the whole peat profile, for the complete MH & CR data set (air-filled, n=60), the predicted mean temperature at the time of the record and appropriate depth, and the redox potential, were most closely associated with the

TABLE 4.46 Summary of correlation coefficients for association between CH_4-C concentration (ppm) and selected variables. Moor House and Coom Rigg. A full description of the variables, with units, is given in Table 4.44.

Depth class (m)	Inflation gas	April data	MED-LAST	Sites	Variables n	pS	E_h	pH	Air	MMAX	MMIN	MMEAN	MHREC	METREC	MHLAST	METLAST	MEDLAST
All	Air	+	-	MH	16	-0,31	-0,21	0,46	0,17	0,10	-0,01	0,05	0,52	0,58	0,38	0,17	-
				CR	44	-0,05	-0,54	0,14	0,20	0,20	0,16	0,19	0,42	0,50	0,33	0,24	-
				MH&CR	60	-0,20	-0,45	0,20	-0,03	0,17	0,10	0,14	0,46	0,53	0,33	0,21	-
All	Air	-	-	MH	6	-0,71	0,10	0,91	-0,50	-0,50	-0,50	-0,50	0,63	0,80	-0,27	-0,57	-
				CR	21	-0,13	-0,60	0,37	-0,09	-0,09	-0,09	-0,09	0,40	0,65	-0,01	-0,43	-
				MH&CR	27	-0,41	-0,41	0,40	-0,32	-0,24	-0,24	-0,24	0,48	0,69	-0,11	-0,48	-
All	N_2	+	-	MH	90	0,45	0,09	0,28	-0,06	-0,11	-0,12	-0,11	-0,40	-0,46	-0,36	-0,39	-
				CR	133	-0,06	-0,07	0,23	-0,04	-0,09	-0,12	-0,10	-0,31	-0,23	-0,35	-0,27	-
				MH&CR	223	0,11	0,03	0,23	-0,14	-0,13	-0,14	-0,13	-0,35	-0,34	-0,34	-0,32	-
0,2,0,5	Air	+	-	MH	6	0,19	0,33	0,31	0,52	0,34	0,44	0,39	0,49	0,05	0,27	0,33	-
				CR	18	0,16	-0,17	-0,33	0,09	0,09	0,09	0,10	0,38	0,30	-0,01	0,01	-
				MH&CR	24	-0,03	-0,03	-0,22	0,04	0,11	0,09	0,10	0,43	0,33	-0,01	0,02	-
0,2,0,5	N_2	+	-	MH	34	0,12	0,27	0,22	-0,03	-0,08	-0,09	-0,09	-0,29	-0,16	-0,18	-0,16	-
				CR	56	0,08	0,15	0,02	-0,18	-0,18	-0,21	-0,20	-0,29	-0,16	-0,32	-0,27	-
				MH&CR	90	0,22	0,32	-0,01	-0,31	-0,21	-0,23	-0,22	-0,31	-0,25	-0,27	-0,28	-
All	N_2	+	+	MH	40	0,48	0,09	0,36	-0,06	-0,10	-0,10	-0,10	-0,71	-0,76	-0,75	-0,75	-0,06
				CR	41	-0,07	0,07	0,49	-0,11	-0,11	-0,11	-0,11	-0,70	-0,56	-0,67	-0,56	-0,11
				MH&CR	81	0,12	-0,00	0,46	-0,12	-0,07	-0,05	-0,07	-0,68	-0,65	-0,67	-0,62	-0,11

TABLE 4.47 Summary of main factors associated with CH_4-C concentration in Moor House and Coom Rigg profiles.

	Air-filled					N_2-filled				
	Temperature		Chemistry			Temperature		Chemistry		
	Peat (°C)	Air (°C)	E_h (mV)	pH (units)	pS (units)	Peat (°C)	Air (°C)	E_h (mV)	pH (units)	pS (units)
Complete profile										
MH	* +			Δ +	Δ −	* −			Δ +	(*) +
CR	(*) +	[Δ] +	* −	[Δ] +		* −			[*] +	
MH&CR	* +	[Δ] +	(*) −	[Δ] +		* −			[Δ] +	
Top 50 cm										
MH	(*) +	* +	Δ +	Δ +		* −			(*) +	
CR	* +			Δ −		* −			[*] +	
MH&CR	* +					(*) −	Δ −	* +		
2.0 m and below										
CR	* ±	[*] +							[*] +	

From correlation analysis
- * most important variable (r>0.25) (possibly jointly so)
- (*) variable showing only slightly less association with CH_4-C concentration than the most important one (within 10% of the highest r value)
- \+ positive association
- Δ important but less so (r>0.25)

[ ] results from regression analyses where these differ, i.e. correlation might be low, but factor consistently accounts for a small percentage of the variation and so r^2 values are significant (included here only if p<0.01)

CH_4-C concentration. The coefficient for the redox potential was -0.45, indicating an increase in CH_4-C concentration with increased reducing properties of the peat, whilst that for the predicted peat temperature was between 0.46 and 0.53, depending on which sine wave equation was used. An increase in CH_4-C concentration was associated equally, but to a small degree, with an increase in total sulphide concentration (r=-0.20 for pS) and an increase in pH (r=0.20). Air temperature was only weakly associated with CH_4-C concentration, correlation coefficients being below 0.20; in particular, the air

temperature at the time of the record gave a coefficient of only -0.03 (and was negative).

At MH the predicted peat temperature at the time of the record gave the highest correlation coefficient (between 0.52 and 0.58), but at CR temperature was slightly less important (maximum r=0.50) than E_h (r=-0.54). The Sites also differed in the relative importance of the chemical factors, thus supporting the assumption that the peat characteristics may be different, as suggested by the gas profile analyses, and the reason for not clumping MH and CR data in ANOVAs. Of the three (pH, pS and E_h), at MH pH was most closely associated with CH_4-C (r=0.46), whilst at CR E_h gave the (overall) maximum correlation coefficient (-0.54).

When N_2 was used to inflate the samplers (n=223), the CH_4-C concentration remained most closely associated with the predicted peat temperature, but the association was *negative*. The same was true for both MH and CR, separately. The correlation coefficient representing the association between CH_4-C concentration and the redox potential fell markedly when N_2 was used. For the MH and CR data set combined it was just 0.03. Of the chemical factors, pH (cf. E_h for air-filled) was the most closely associated with CH_4-C concentration when all data were combined, yielding a coefficient of 0.23, but again the two Sites varied in the relative importance of the chemical factors.

Over the top 50 cm of the profile, E_h showed an equally close association with CH_4-C concentration as peat temperature when N_2 was used, but showed no such close association when air was used. In contrast, over the whole profile, E_h and temperature were equally associated with CH_4-C concentrations when air was used, but temperature prevailed when N_2 was used.

Data from 2.0 m and 4.0 m at sites 13, 14 and 15 at CR were used to assess the importance of the selected variables deep in the peat profile. The data sets were small ($5 \leq n \leq 9$), and the variation in the correlation coefficients large. However, it was clear from the results that at these depths temperature remained the factor most closely associated with CH_4-C concentration, although there was no consistency about which temperature variable specifically (or whether positive or negative). Similarly, of the three chemical variables

tested, there was no consistency between the sites as to which was the most important. The results were the same whether air or N_2 had been used to inflate the samplers.

A comparison of the correlation coefficients for individual sampling sites indicated certain consistencies, but also highlighted much variation between them. Analyses were carried out on the complete profile, and on the top 50 cm. Insufficient data were available for individual site data from deep peat to be used. Except at site 17 when air had been used to fill the samplers, all sites indicated that the predicted peat temperature was most closely associated with CH_4 concentration, and that, except at site 15, the association was positive when air was used, and negative when for N_2-filled samplers. At site 17 (all depths) air temperature gave the highest correlation coefficients. At MH the relative importance of pS, E_h and pH at each of the three sites was consistent for any analysis (data set), but this was not the case for the five CR sites.

It is evident from the preceding account that temperature, and more often that of the peat than that of the air, is most closely associated with the concentration of CH_4-C in the peat. The nature of the association changed with the gas used to inflate the samplers. At least one of the three chemical variables (pH, pS and E_h) was usually of secondary importance, but the precise details varied with the gas used for inflation (particularly its effect on the E_h correlation coefficient) and, sometimes, the depth. There were also discrepancies in detail between MH and CR results in this respect.

In order to assess the significance of these associations and the reliability of the inferences made, linear regressions were carried out for the CH_4-C concentration on each of the eleven independent variables (MEDLAST omitted) in turn. Those which returned significant ($p<0.05$) equations are shown in Appendix Nb.

The results show that, as expected from the correlation coefficients, the predicted peat temperatures gave the most significant regressions, with little difference between those for the time of the record and those for the period since the previous field visit. Where other variables gave rise to equally significant

regression equations, the proportion of the variation in CH_4-C concentration accounted for was smaller, with one exception.

Peat temperature was significant in the regressions based on data from the entire profile and on those representing the top 50 cm of peat, but there were no significant peat temperature variable regressions for depths below 2.0 m. Although temperature regressions were significant, they acounted for less than 25% of the variation in CH_4-C concentration, and in most cases for less than 20%. Of the total of 73 significant regressions, 24 accounted for less than 10% of the variation, 61 for less than 20%, and 12 for 20% or more. In general, then, any one variable cannot be used to predict the changes in CH_4-C concentration accurately.

The second most important variable overall was pH. It was noteably unimportant in the top 50 cm of peat, but was significant at least below 2.0 m, and over the entire profile it accounted for between 7% ($p<0.01$) and 79% ($p<0.001$) of the variation in CH_4-C concentration.

None of the variables was clearly associated with the concentration of CH_4-C in the top 50 cm of peat to any large extent, though all but pH returned small (and significant) r^2 values of between 0.05 and 0.14 when N_2 was used as the inflation gas. When air was used there was no close association.

None of the three monthly mean air temperature variables were more closely associated with the CH_4-C concentration than the others, so that nothing would be gained by knowing more than one for the purposes of calculating regression equations.

As already noted, the correlation coefficients indicated a large drop in the degree of association between the CH_4-C concentration and redox potential over the entire profile when N_2 was used to fill the samplers in place of air, but an increase in the association in the top 50 cm (and the association there was positive rather than negative). However, the number of significant regressions for CH_4-C concentration on E_h was very low, and they accounted for, at most, only 11% of the variation. In an attempt to clarify any such association, a series of linear regressions was carried out using data

from only one field visit for each analysis. It was hoped that such an approach would make clear what rôle E_h played, allowing any seasonal trends, and contrasts between N_2- and air-filled sampler data, to be seen. The results are shown in Table 4.48. Redox

TABLE 4.48 Summary of significant regressions of CH_4-C concentration on redox potential, E_h. Coefficients of determination and significance levels for linear regression equations. Empty cells represent non-significant results.

Depth class (m)	Site		Air-filled Apr 1982	May 1982	Jun 1982	Aug 1982	N_2-filled Sep 1982	Oct 1982	Dec 1982	Apr 1983	May 1983	Jun 1983	Aug 1983	Sep 1983
All	MH	n	12	12	6	-	12	12	12	12	12	12	9	12
		r^2		0,46			0,42						0,52	
		sig.		*			*						*	
	CR	n	20	19	17	19	19	19	17	18	10	19	19	20
		r^2	0,2	0,55	0,29		0,25							
		sig.	*	***	*		*							
	MH & CR	n	32	31	23	19	31	31	29	30	22	31	29	32
		r^2	0,18	0,34			0,31							
		sig.	*	**			***							
0,2,0,5	MH	n	6	6	6	-	6	6	6	6	6	6	6	6
		r^2					0,95	0,91						
		sig.					*	*						
	CR	n	10	10	10	10	10	10	10	10	10	10	10	10
		r^2		0,82	0,46	0,57	0,62		0,59		0,53	0,81	0,94	0,67
		sig.		**	*	*	*		*		*	**	***	*
	MH & CR	n	16	16	16	10	16	16	16	16	16	16	16	16
		r^2		0,61			0,65	0,39			0,37		0,46	
		sig.		*			**	*			*		*	
2,0-3,0	MH	n	6	6	0	-	6	6	5	6	6	6	3	6
		r^2												
		sig.												
2,0-5,0	CR	n	10	9	7	9	9	9	7	8	0	9	9	10
		r^2							0,55					
		sig.							*					
2,0-5,0	MH & CR	n	16	15	7	9	15	15	13	14	6	15	12	16
		r^2												
		sig.												

potential was apparently more important in the summer months, especially during the period of rapid increase in CH_4-C concentration and its peak time, but the significant regressions were not confined to the warmest months only. The number of significant regressions based on data from the whole profile dropped dramatically when N_2 was used for inflation rather than air, except that the first set of samples from N_2-filled samplers gave significant results. In the top 50 cm of the peat at CR, the significance of the redox potential appeared to fall between May and August when air was used, whereas in the same months the following year, when N_2 was used, the significance and the amount of variation accounted for increased. No significant regressions were returned for the top 50 cm of peat at MH over this period, and redox potential was of no significance below 2.0 m at either site.

Stepwise 'model' multiple regression analyses were carried out on MH and CR data together, for the complete profile, the 0.2-0.5 m depth class and the >2.0 m depth class. The models regressed CH_4-C concentration on pS, E_h and pH simultaneously to see whether a multivariate approach would improve the corresponding single-variable regressions. The second step added the spot air temperature to the regression, followed by the best temperature variable, 'best' being interpreted as the significant ($p<0.01$) variable which returned the highest r^2 value in the individual variable linear regression analyses described above (and see Appendix Nb). Table 4.49 shows the regression statistics (r^2 and significance level), and Appendix Nc gives the full set of regression parameter values.

The model linear regressions for the full profile were all highly significant ($p<0.01$) and accounted for between 8% and 36% of the variation in CH_4-C concentration. Using the data from samplers which had been filled with air, pS, E_h and pH accounted for 26% of the variation ($p<0.001$), compared with only 8% ($p<0.001$) using data from N_2-filled samplers. In both cases the addition of the spot air temperature to the regression did not significantly improve the r^2 value, but addition of the most significant temperature variable, METREC, did so.

TABLE 4.49 Summary statistics for model linear multiple regressions of CH_4-C concentration (ppm) on pS, E_h, pH and spot air temperature, plus the 'best' significant temperature variable from the individual variable regression analyses. For further details see text. Regression estimates given in Appendix Nb. A full description of the variables, with units, is given in Table 4.44. MH and CR data together.

Depth class (m)	Inflation gas	pS	E_h (mV)	pH	(spot) air temp. (°C)	'best' temp. (°C)	Regression r^2	statistics sig.
All	Air	+	+	+			0.26	***
		+	+	+	+		0.26	**
		+	+	+	+	+	0.36	***
All	N_2	+	+	+			0.08	***
		+	+	+	+		0.10	***
		+	+	+	+	+	0.21	***
		+	+	+	+	+	0.21	***
0.2,0.5	Air	+	+	+				ns
		+	+	+	+			ns
0.2,0.5	N_2	+	+	+			0.10	*
		+	+	+	+		0.17	**
2.0-5.0	Air	+	+	+				ns
		+	+	+	+			ns
2.0-5.0	N_2	+	+	+				ns
		+	+	+	+			ns

Of the multiple regressions based on data from shallow and deep parts of the profile, respectively, only that using data from N_2-filled samplers at 0.2 m and 0.5 m was significant. The regression on pS, E_h and pH was significant only at the $p<0.05$ level ($r^2=0.10$) and the values were improved to $p<0.01$ and $r^2=0.17$ when the spot air temperature was included.

CARBON DIOXIDE

As for CH_4-C, correlation and regression analyses to determine the factors most closely associated with CO_2-C concentration gave complex results from which it is difficult to draw general, accurate conclusions with confidence. Table 4.50 is an attempt to represent the main features arising from the analyses in such a way that general

TABLE 4.50 Summary of main factors associated with CO_2-C concentration in Moor House and Coom Rigg profiles.

	Air-filled					N_2-filled				
	Temperature		Chemistry			Temperature		Chemistry		
	Peat (°C)	Air (°C)	E_h (mV)	pH (units)	pS (units)	Peat (°C)	Air (°C)	E_h (mV)	pH (units)	pS (units)
Complete profile										
MH	* +	[*] +				* -				(*) +
CR	* +	(*) +	(*) -							
MH&CR	* +	Δ[*] + +	Δ -							
Top 50 cm										
MH	(*) +	* +	Δ +						* +	
CR	Δ +	[*] +		* +	Δ +			* +		
MH&CR	* +	Δ +		Δ -				* +		
2.0 m and below										
CR	* ±	* ±							* -	

From correlation analysis
- * most important variable (r>0.25) (possibly jointly so)
- (*) variable showing only slightly less association with CH_4-C concentration than the most important one (within 10% of the highest r value)
- \+ positive association
- Δ important but less so (r>0.25)

[ ] results from regression analyses where these differ, i.e. correlation might be low, but factor consistently accounts for a small percentage of the variation and so r^2 values are significant (included here only if p<0.01)

comparisons can be made quickly, as Table 4.47 for CH_4-C. Table 4.51 shows the correlation coefficients resulting from analysis of the CO_2-C concentrations and the selected variables in Table 4.44.

It appears from the coefficients that air temperature is more closely associated with CO_2-C concentration than was the case for CH_4 C, but that peat temperature is also important, perhaps more so deeper in the peat. When N_2 was used to fill the samplers in place of air, the importance of temperature appeared to fall to insignificant

TABLE 4.51 Summary of correlation coefficients for association between CO_2-C concentration (ppm) and selected variables. Moor House and Coom Rigg. A full description of the variables, with units, is given in Table 4.44.

Depth class (m)	Inflation gas	April data	MED-LAST	Sites	Variables n	pS	E_h	pH	Air	MMAX	MMIN	MMEAN	MHREC	METREC	MHLAST	METLAST	MEDLAST
All	Air	+	-	MH	16	-0,08	-0,12	-0,20	0,04	0,12	0,10	0,11	0,46	0,40	0,40	0,26	-
				CR	46	0,10	-0,31	-0,01	0,29	0,29	0,30	0,30	0,27	0,32	0,15	0,02	-
				MH&CR	62	0,01	-0,27	0,02	0,14	0,24	0,24	0,25	0,32	0,34	0,22	0,09	-
All	Air	-	-	MH	6	-0,24	0,29	0,35	-0,04	-0,04	-0,04	-0,04	0,44	0,35	-0,11	-0,15	-
				CR	22	0,14	-0,33	0,29	0,17	0,17	0,17	0,17	0,20	0,40	0,01	-0,34	-
				MH&CR	28	-0,01	-0,23	0,27	-0,02	0,10	0,10	0,10	0,26	0,38	-0,04	-0,30	-
All	N_2	+	-	MH	90	0,31	0,23	0,22	0,02	0,07	0,09	0,08	-0,34	-0,35	-0,23	0,22	-
				CR	133	0,20	0,19	0,01	0,01	0,05	0,08	0,07	0,03	0,06	0,05	0,10	-
				MH&CR	223	0,22	0,20	0,03	-0,06	0,03	0,05	0,04	-0,03	-0,01	0,01	0,04	-
0,2,0,5	Air	+	-	MH	6	0,16	0,38	0,08	0,57	0,56	0,59	0,58	0,56	0,02	0,44	0,52	-
				CR	18	0,25	-0,14	-0,33	0,11	0,11	0,15	0,13	0,27	0,17	0,05	0,07	-
				MH&CR	24	0,14	-0,01	-0,27	0,22	0,21	0,25	0,23	0,33	0,15	0,14	0,18	-
0,2,0,5	N_2	+	-	MH	34	-0,11	0,20	0,35	-0,19	-0,10	-0,05	-0,08	-0,21	-0,19	-0,05	-0,10	-
				CR	56	0,15	0,27	0,18	0,06	0,13	0,14	0,14	0,12	0,13	0,14	0,13	-
				MH&CR	90	0,18	0,31	0,15	-0,08	0,06	0,07	0,07	0,04	0,03	0,08	0,06	-
All	N_2	+	+	MH	40	0,45	0,22	0,29	0,03	-0,02	-0,04	-0,03	-0,68	-0,68	-0,65	-0,62	0,03
				CR	41	0,13	-0,00	0,32	0,10	0,10	0,10	0,10	-0,59	-0,39	-0,59	-0,35	0,10
				MH&CR	81	0,13	0,02	0,38	-0,03	0,07	0,09	0,08	-0,60	-0,52	-0,55	-0,44	0,03

levels, and that of the redox potential dropped and became positive. Further, when N_2 was used to fill the samplers, the chemical variables were relatively more important than those of temperature in the top 50 cm of peat, as well as over the whole profile, and of these the redox potential gave the highest correlation coefficient.

Comparison between the correlation coefficients for the whole profile of individual sampling sites revealed variation between them in the relative importance of temperature and chemical variables, and between that of the individual variables within each group. Noteworthy was the contrast in the relative importance of the temperature variables at sites 13 and 17. At site 13 the predicted peat temperatures gave correlation coefficients between one and six times larger than those for the air temperatures, but at site 17 the air temperature was slightly more closely associated with the CO_2-C concentration than was peat temperature, over the whole profile. Furthermore, the association between the air temperature and the CO_2-C concentration was positive at site 13, and negative at site 17. These results are similar to those for CH_4-C correlation coefficients. Such contrasts may not be significant, however, since there was no apparent trend in the relative importance of air and peat temperatures in sites 14, 15 and 16 with the position of the site on the bog or the total depth of the profile.

Appendix Nc gives the level of significance and the amount of variation accounted for by all the significant ($p<0.05$) linear regression equations of CO_2-C concentrations based on the individual selected variables used for the correlation analyses. It allows an assessment of the reliability of the features highlighted by the preceding comparison of the correlation coefficients. It is clear from the appendix that, for the full profile, air temperature (both spot and monthly mean values) was most closely associated with the CO_2-C concentration, out of the eleven variables tested. This contrasts with the situation for CH_4-C, where the peat temperature was more important. Over the entire profile, peat temperature was also significant ($p<0.05$), but accounted for 11% or less of the variation compared with between 16% and 44% accounted for by air temperature variables ($p<0.01$). At CR the relative importance of the air

temperature to that of the peat temperature was about ten-fold more, compared with two- or three-fold at MH.

Regression equations based on the chemical variables were of lower significance and accounted for less of the variation in CO_2-C concentration, on the whole (r^2=0.19) than the temperature variables. No one of the three was consistently more important than the others, as was the case for CH_4-C concentrations. The importance of the redox potential increased from insignificance to the $p<0.01$ level when N_2 was used to inflate the samplers in place of air, but was insignificant below 2.0 m.

Data were treated to linear regression analysis of CO_2-C concentration on redox potential for each field visit in turn, as had been done for CH_4-C. The results are shown in Table 4.52.

As for the corresponding CH_4-C regressions, none were significant which were based on data from 2.0 m and below, and more significant results were returned for the 0.2-0.5 m part of the profile than for the whole. Beyond this it is difficult to draw conclusions from the results. Of a total of 21 significant regressions, only six were significant at the $p<0.01$ level or better, and of these, two represented regressions based on data from air-filled samplers positioned between 0.2 m and 0.5 m in June and August 1982 at CR, and the remaining four represented regressions based on N_2-filled samplers. Of these four, two were also based on data from 0.2 m and 0.5 m at CR, but for October and December, 1982; the final two significant regressions were for the entire profile at CR in December 1982 and for the full profile at MH in August 1983.

A summary of the statistics from a multiple regression approach to the problem of determining the important factors associated with CO_2-C concentration are shown in Table 4.53. The full set of regression estimates are given in Appendix Nd. They refer to stepwise model linear regressions of CO_2-C concentration on chemical and temperature variables, as previously described for CH_4-C, above.

In general, the concentrations of CO_2-C in the peat were less well described by this means than was the case for CH_4-C concentrations. For data representing the complete profile, those

TABLE 4.52 Summary of significant regressions of CO_2-C concentration on redox potential, E_h. Coefficients of determination and significance levels for linear regression equations. Empty cells represent non-significant results.

Depth class (m)	Site		Air-filled Apr 1982	May 1982	Jun 1982	Aug 1982	N_2-filled Sep 1982	Oct 1982	Dec 1982	Apr 1983	May 1983	Jun 1983	Aug 1983	Sep 1983
All	MH	n	12	12	6	-	12	12	12	12	12	12	9	12
		r^2											0.72	
		sig.											***	
	CR	n	20	19	17	19	19	19	17	18	10	19	19	20
		r^2		0.21	0.22				0.37	0.19			0.22	
		sig.		*	*				**	*			*	
	MH & CR	n	32	31	23	19	31	31	29	30	22	31	28	32
		r^2		0.17						0.11				
		sig.		*						*				
0.2,0.5	MH	n	6	6	6	-	6	6	6	6	6	6	6	6
		r^2					0.96	0.94						
		sig.					*	*						
	CR	n	10	10	10	10	10	10	10	10	10	10	10	10
		r^2			0.74	0.87	0.89	**	0.84	0.63	0.56	0.58	0.64	0.60
		sig.			**	***			***	*	*	*	*	*
	MH & CR	n	16	16	16	10	16	16	16	16	16	16	16	16
		r^2									0.33		0.35	
		sig.									*		*	
2.0-3.0	MH	n	6	6	0	-	6	6	6	6	6	6	3	6
		r^2												
		sig.												
2.0-5.0	CR	n	10	9	7	9	9	9	7	8	0	9	9	10
		r^2												
		sig.												
2.0-5.0	MH & CR	n	16	15	7	9	15	15	13	14	6	15	12	15
		r^2												
		sig.												

collected from air-filled samplers could not be predicted in terms of pS, E_h, pH and air temperatures, and those from N_2-filled samplers gave only marginally better results, accounting for only 7% of the variation. The maximum r^2 values obtained in these analyses was 0.12.

TABLE 4.53 Summary statistics for model linear multiple regressions of CO_2-C concentration (ppm) on pS, E_h, pH and spot air temperature, plus the 'best' significant temperature variable from the individual variable regression analyses. For further details see text. Regression estimates given in Appendix Nd. A full description of the variables, with units, is given in Table 4.44. MH and CR data together.

Depth class (m)	Inflation gas	pS	E_h (mV)	pH	(Spot) air temp. (°C)	'best' temp. (°C)	Regression r^2	statistics sig.
All	Air	+	+	+				ns
		+	+	+	+			ns
		+	+	+	+	+		ns
		+	+	+	+	+		ns
		+	+	+		+		ns
All	N_2	+	+	+			0.07	**
		+	+	+	+		0.07	**
0.2,0.5	Air	+	+	+				ns
		+	+	+	+			ns
0.2,0.5	N_2	+	+	+			0.12	*
		+	+	+	+		0.12	*
2.0-5.0	Air	+	+	+				ns
		+	+	+	+			ns
2.0-5.0	N_2	+	+	+			0.10	*
		+	+	+	+			ns

This summary clearly indicates the complex (and not always consistent) variation in the apparent effects of temperature and other peat characteristics on the concentration of CH_4-C and CO_2-C. Associations identified from a given data set are not generally applicable to another, and vary with site, depth and sampling methodology.

4.4 CHEMICAL CHARACTERISTICS OF PEAT PROFILES

4.4.1 INTRODUCTION

The present section describes the quantitative changes in pH, redox potential and total sulphide concentration (S^{2-}), and the movement of the upper limit of the (semi-quantitative) sulphide zone.

with respect to depth in the peat and temperature. After separate analysis of pH, redox potential and sulphide concentration data, a (linear) multiple regression approach is used to determine the most important factors connected with total sulphide concentration and their relative significance at different depths.

Measurements were made at MH and CR on each field visit between October 1981 and September 1983 (Table 4.54). Visits prior to March 1982 yielded incomplete sets of profile data, only some of which were considered to be reliable and were included in the analyses. From March 1982 all data collected were used, but on two occasions problems with the equipment prevented one or more of the three profiles being measured.

In choosing the location for this work on each visit, an effort was made to find a suitable site for coring as close as possible to those areas from which gases were being collected, whilst avoiding disturbance to the gas samplers by being too close. Initially, proximity to a gas collection site was considered most important, and the earlier cores were taken from a range of nearby habitat types. After several trips it was clear that variations in total peat depth, water level and the depth of the upper limit of the humified layer (acrotelm/catotelm boundary) were considerable, even over short distances of up to 6 m. From September 1982 it was decided to core in areas which were comparable in terms of their surface vegetation (i.e. microhabitat type); thereafter all measurements were made below lawns at MH and their closest equivalent at CR. Because of surface trampling and disturbance to the peat profile when coring, it was necessary to work in a fresh area on each visit, and because of the restriction placed on the microhabitat to be used, the distance of the coring site from the gas collection sites tended to increase. However, having imposed the microhabitat restriction, searches were always made from the same gas collection point at each Site; site 3 at MH and site 14 at CR. The maximum distance recorded was 15 m. Thus, the sample profiles were selected for comparability as far as possible in the field, but despite this attempt at a degree of standardisation, an examination of the results revealed no decrease in the variation in the depth of the water level or the upper limit of the humified layer,

TABLE 4.54 Location of coring sites for pH, redox potential and sulphide concentration profile measurements.

Date	Location and microhabitat	Records made pH	E	S^{2-}
a) Moor House				
02,10,81	5 m from sites 4-6	(+)	(+)	(+)
	5 m from site 3	(+)	(+)	(+)
31,03,82	Between Conway exclosure and sites 1-2, Hummock	+	+	+
05,05,82	Hummock	+	+	+
21,06,82	Adjacent to site 2, Hummock	+	+	+
18,08,82	Adjacent to site 3, Dry	+	-	-
23,09,82	15 m from sites 4-6, Lawn	+	+	+
24,10,82	12 m from site 3, Lawn	+	+	+
06,04,83	7 m from site 3, Lawn	+	+	+
14,05,83	4 m from site 3	+	+	+
21,06,83	10 m from site 3, Dry lawn/low hummock	+	+	+
31,07,83	14 m from site 3, Lawn	+	+	+
17,09,83	10 m from site 3, Lawn	+	+	+
b) Coom Rigg				
29,11,81	6 m from site 14, Wet	(+)	-	(+)
01,04,82	Adjacent to site 14, Low hummock	+	+	+
03,05,82	Adjacent to site 14, Hummock	+	+	+
20,06,82	Adjacent to site 14, Hollow	+	+	+
22,06,82	Adjacent to site 15, Hummock	+	+	+
17,08,82	Adjacent to site 14, Lawn	+	+	-
19,08,82	Not recorded	-	+	-
22,09,82	10 m from site 14, Wet lawn	+	+	+
23,10,82	8 m from site 14, Wet lawn	+	+	+
11,12,82	6 m from site 14, Wet lawn	+	+	+
13,12,82	7 m from site 14, Wet lawn	+	+	+
05,04,83	6 m from site 14, Wet lawn	+	+	+
13,05,83	10 m from site 14, Wet lawn	+	+	+
20,06,83	3 m from site 14, Wet lawn	+	+	-
29,07,83	14 m from site 14, Lawn	+	+	+
16,09,83	15 m from site 14, Wet lawn	+	+	+

( ) denotes incomplete record

relative to the surface or to each other, when the microhabitat restriction was imposed. The variation in all of these factors was considerable, even when the seasonal factor was removed and adjacent 'duplicate' coring sites were compared. Hence, in the analyses which follow, it is assumed that the change in the coring site selection

procedure had only an insignificant effect, and all the data have been treated in the same way. More details of the local variation in selected peat characteristics have been given in Chapter 2.

Prior to any analysis, some preliminary preparation of the raw field data was necessary. Values of pH were corrected for any meter drift over the period of measurement, as detected from a comparison of glass electrode calibrations in pH 4 and pH 7 standard solutions before and after each coring session of four to five hours. Redox potential measurements (E) were corrected to the equivalent hydrogen electrode potential (E_h) by addition of 268 mV to the field reading. In addition, the Pye Unicam pH meter mV response in unconventional, and results in a reversal of the usual polarity of the response, so it was necessary to correct for this by reversing the sign of the mV reading. To calculate the total peat sulphide concentrations from the field data (mV) several steps were involved. The concentration of the weekly sulphide standard used in the field was determined from the results of the laboratory standardisations carried out prior to each field visit. The electrode slope was calculated, using the change in mV readings corresponding to decade concentration changes in standard sulphide solutions. These data were collected in the field prior to each coring session. Then, the calibration curve was obtained from the field measurement of the weekly sulphide standard electrode potential and the electrode slope. Finally, from the calibration curve for each coring session, it was possible to convert the field-measured electrode potential to the corresponding total sulphide concentration. (Strictly, the Ag/S electrode measures free sulphide activity, but by using the SAOBII buffer, which contains a high concentration of OH^- ions, all sulphide species are in the form of S^{2-}. At the concentrations encountered, activity is almost equivalent to concentration (see Section 3.1.4, Quantitative Sulphide Measurements, and Appendix F). Details of the sulphide calculations are given in Appendix H. All weekly sulphide standards fell within the S^{2-} concentration range 9 to 14 mmol dm^{-3} (at equivalent dilution to that of peat samples).

The data for each of the three variables pH, redox potential (E_h), and the total sulphide concentration (S^{2-}), were grouped into

depth and date classes for analysis of variance. Multiple regression analyses were carried out using individual data items. In the following accounts, the results of the analyses of variance are treated separately for each variable, followed by the results of the multiple regression analyses. Finally, some features of the sulphide concentration changes in the top 25 cm of the peat are described in terms of the water level and the upper limit of the humified layer.

4.4.2 pH PROFILES

The pH measured in selected garden peat cores on four occasions between October and December 1983 are shown in Table 4.55. These may be compared with the MH pH values, the majority (>75%) of which were between pH 3.00 and pH 4.99, apparently indicating no significant change in pH since collection from the field three years earlier. M1 values were slightly higher (pH 4.1 and pH 4.6).

TABLE 4.55 pH of garden peat cores. pH measured at the water level in representative cores as shown, on each of the last four gas sampling dates.

	31.10.83	16.11.83	29.11.83	12.12.83
P1	4.5	4.6	4.0	4.0
L1	3.4	3.7	3.7	3.9
H1	3.6	3.7	3.7	3.6
M1	-	-	4.6	4.1

Profiles of pH were recorded at MH and CR on every visit between October 1981 and September 1983, representing all months of the year except January and February (Table 4.54). The seasonal distribution of the records is shown in Table 4.56. Timing of the field trips and the number of daylight hours available were the main contributory factors to the unequal distribution of the records. The number of pH measurements made varied between 5 and 9 per block, and between 6 and 24 for each profile.

Fig. 4.58 has been drawn using all the collected data to illustrate the general acidity of the peat at the field Sites irrespective of season or depth, and to allow a comparison between MH

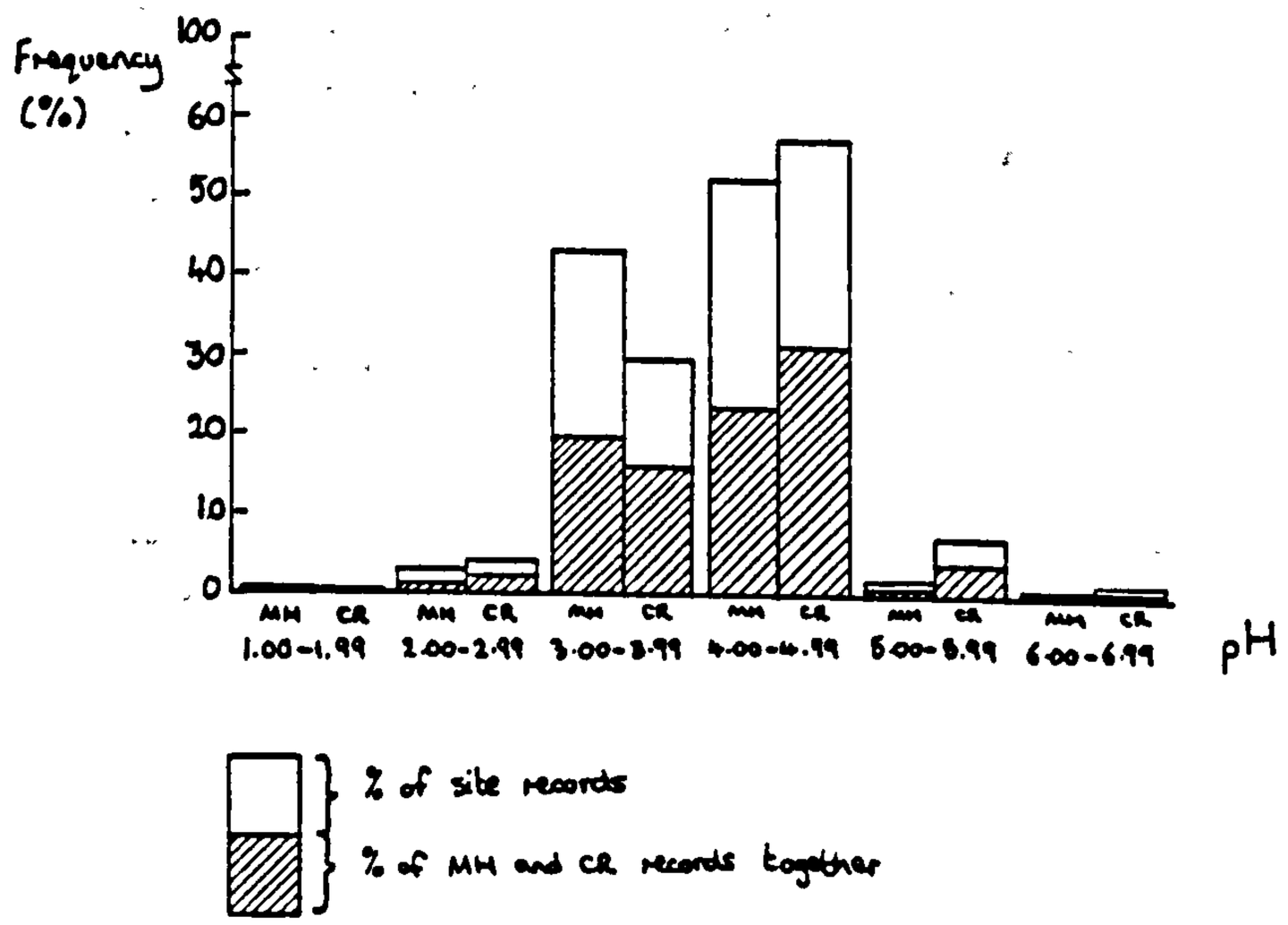
TABLE 4.56 Seasonal distribution of pH profiles recorded at Moor House and Coom Rigg.

	Jan		Feb		Mar		Apr		May		Jun		Jul		Aug		Sep		Oct		Nov		Dec	
	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P
MH	0	0	0	0	1	1	2	1	3	3	3	3	2	2	1	0	3	3	1	1	0	0	0	0
CR	0	0	0	0	0	0	2	2	3	2	3	4	2	2	1	1	3	3	1	1	0	1	2	2

B = number of blocks recorded (0 to -30 cm)
P = number of deep profiles recorded (-50 cm to base of peat)

and CR peat. The Figure shows the percentage of records at each Site falling within the pH ranges indicated, and suggests a slightly higher acidity at MH. At both Sites the highest percentage of records was in the range pH 4.00 to pH 4.99 and more than 75% of the records were between pH 3.00 and pH 4.99. The pH 1.9 value was measured at -20 cm and is very low. It was checked in the field but repeated readings were consistent. The pH was 3.1 at -15 cm, and at -20 cm in the adjacent, duplicate, profile the pH was 3.1. Both -20 cm records

FIG. 4.58 Acidity of peat at Moor House and Coom Rigg



represented peat (5 cm below the onset of the humified zone (black horizon) and were 13-14 cm below the water level. It is interesting, though probably not significant, that the lowest pH recorded at CR (pH 1.95) was also recorded on the April 1983 field visit, on the day prior to that at MH. The record was made at -45 cm: that is, 28 cm below the onset of the humified zone and 39 cm below the water level. These were the only two pH values recorded less than pH 2.0, and are included for the sake of objectivity. There is no way of verifying them. It is conceivable that, given a sudden, large, drop in water level which would allow the sulphides present to be oxidised, the pH might be reduced significantly. However, this cannot be the case here, since both records were made several centimetres below the water level, and there is no reason for believing that it had been much lower prior to the field visit.

FIG. 4.59 Seasonal change in frequency of individual classes of pH records

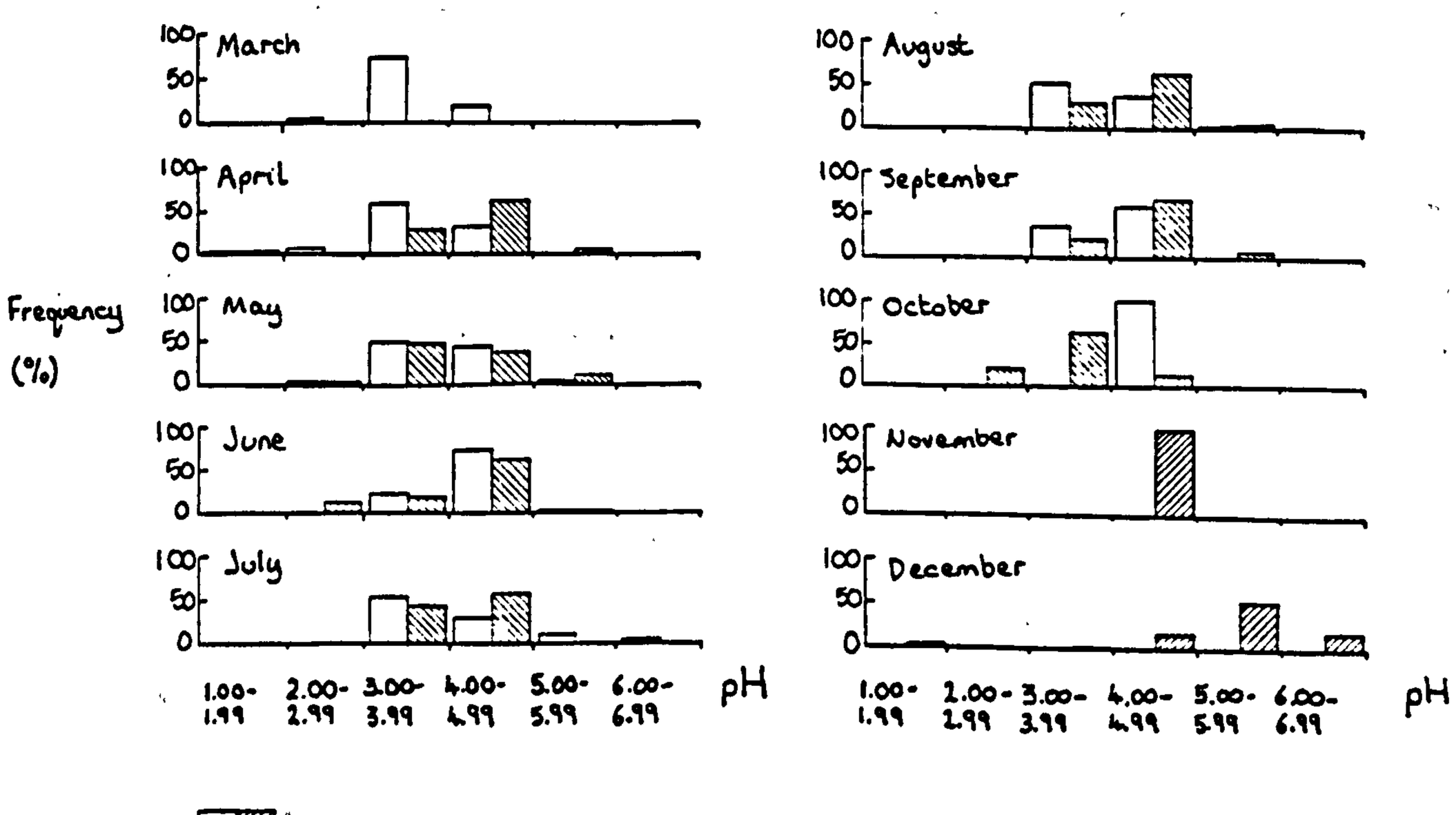


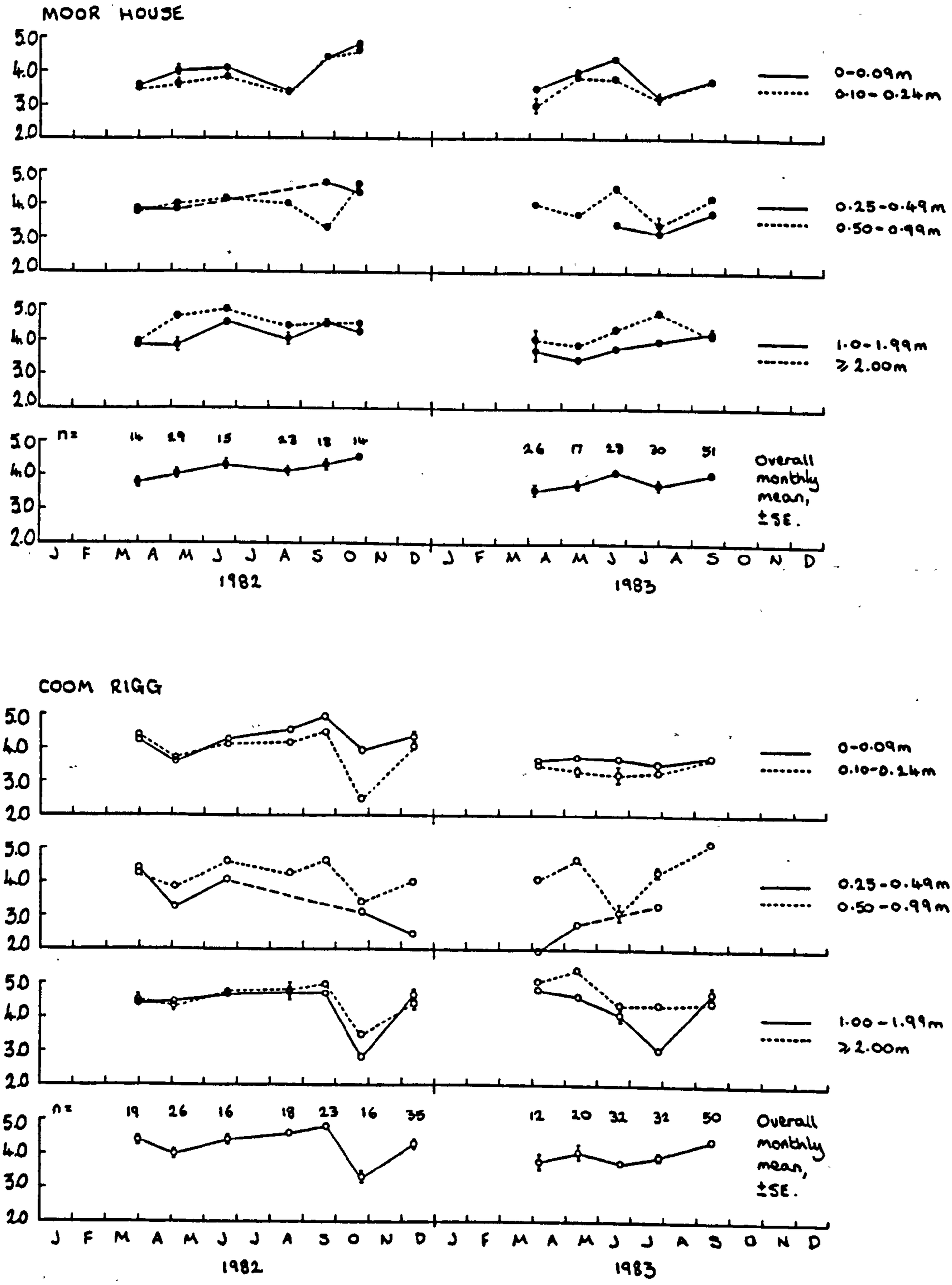
Fig. 4.59 shows the distribution of the pH records for each Site for each month, and illustrates the complexity of the changes. The spread of the entire data sets varied from one month to the next.

Fig. 4.60 summarises the seasonal change in pH at MH and CR, based on the monthly mean pH. The pH showed small, but consistent, changes over both seasons at both Sites. The mean variation within each season for all depths combined was less than 1.0 pH unit, with the exception of October 1982 at CR, where the pH dropped 1.5 pH units. However, a similar fall was seen simultaneously at all depths and may be methodological. In general, the pH increased by 0.5-1.0 unit over the early part of the season and into summer, when there was a small drop and a subsequent recovery into the autumn. Although only small, the changes are consistent, and appear to be significant, as judged by the standard errors. The timing of the maxima and minima was similar in both years at MH, but varied at CR, and did not coincide at the two Sites in either year.

At MH, changes coinciding with those at the surface occurred down to at least 24 cm in 1982, and down to 1 m in 1983. Below this, seasonal changes occurred but the range was smaller and the changes were not consistent between years. In the top 10 cm the seasonal range was about 1.5 pH units, compared with about 0.7 pH units between 1.00-1.99 m. Below this, to the base of the peat, the seasonal range increased again to about 1.0 pH unit, possibly in connection with an increase in mineral content in the basal peat. The CR pH records were more erratic than those from MH, although the mean monthly values for all depths combined showed the same relative changes as those at MH.

A series of analyses of variance were carried out to determine the significance of the seasonal pH changes at different depths. The depth classes employed were narrower than those used for Fig. 4.60, to allow a higher resolution analysis. Eleven analyses were completed, each looking at a different range of depth classes. The results are shown in Table 4.57 (p. 285). Moor House and CR data were clumped together. The top 10 cm showed no significant seasonal change in pH, as might be expected because of the large variation in the data set

FIG. 4.60 Seasonal changes in pH at Moor House and Coom Rigg, 1982-1983. Mean values (±SE where n>6) (1≤n≤20)



when MH and CR data are clumped. All profiles covering a range of depths from the surface to -100 cm which were tested for a seasonal change in pH gave a significant result at the $p<0.05$ level except the 0-10 cm and the 0-20 cm profiles. Profiles over a range of depths upwards from the base of the peat to -50 cm showed no significant seasonal change in pH. Thus, it is clear that most seasonal changes occur over the top 50 cm, and to a lesser extent between 50 cm and 100 cm.

TABLE 4.57 Summary of results from analyses of variance of seasonal and depth changes in pH, redox potential and pS at Moor House and Coom Rigg.

Results of ANOVAs on MH & CR data together.

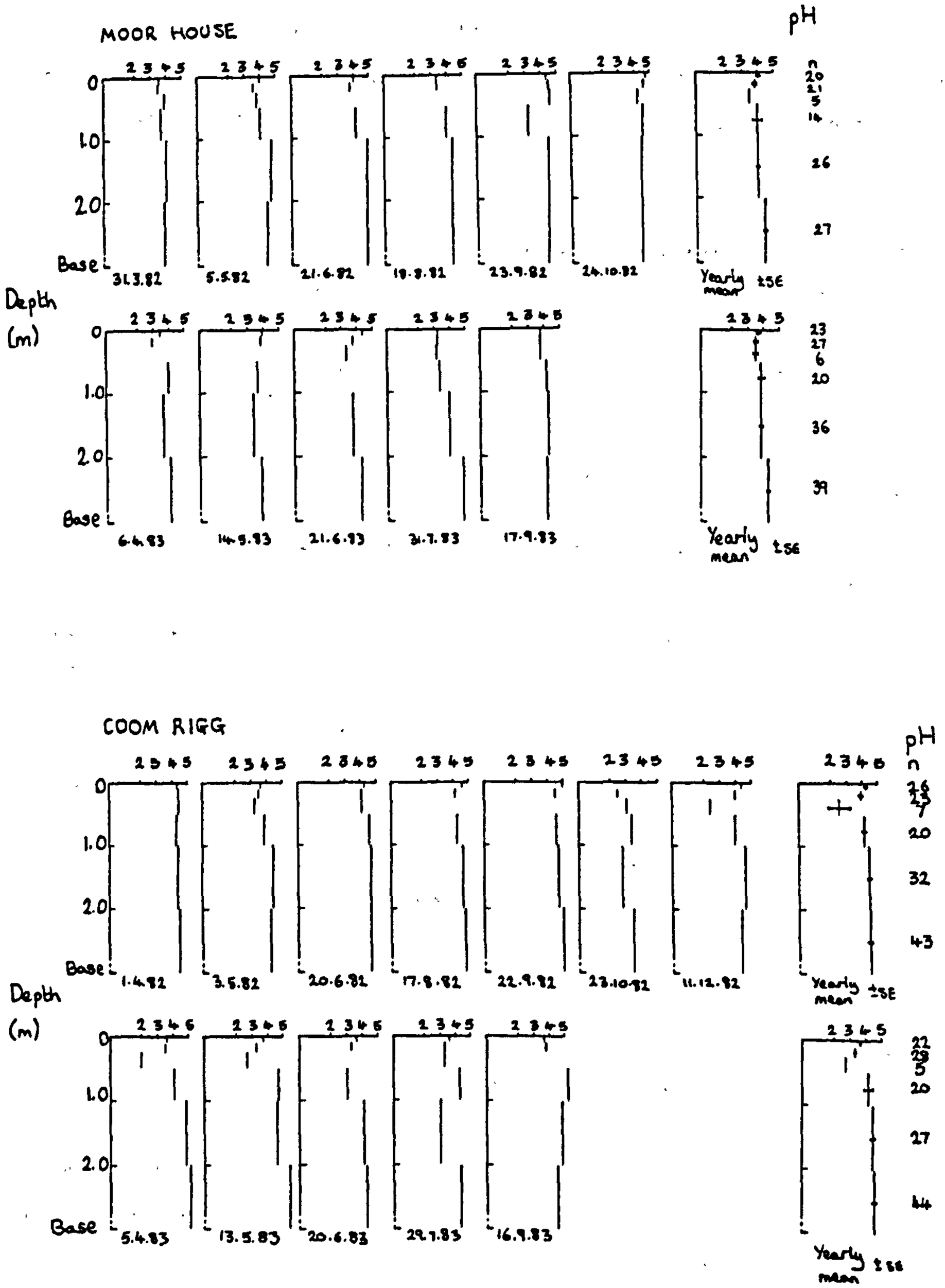
Depth range tested (m)	pH		E_h		pS	
	Date	Depth	Date	Depth	Date	Depth
0.00-5.00	*	***†	***†	***	***	*
0.00-0.10	ns	ns	***	***	ns	ns
0.00-0.15	*	ns	***†	***†	*	**
0.00-0.20	ns	ns	***†	***†	**	***
0.00-0.25	*	ns	***†	***†	**	***
0.00-0.50	*	*	***†	***†	***	***
0.00-1.00	*	*	***†	***†	***	***†
0.50-5.00	ns	**	***	ns	***	ns
1.00-5.00	ns	**	***†	ns	***†	ns
1.50-5.00	ns	ns	***†	ns	***	ns
2.00-5.00	ns	ns	***†	ns	***	ns

† $p<0.0001$

Turning to the effect of depth on the peat pH, irrespective of season, the overall changes were apparently more straightforward than those of season, and were consistent between MH and CR (Figs. 4.61 and 4.62).

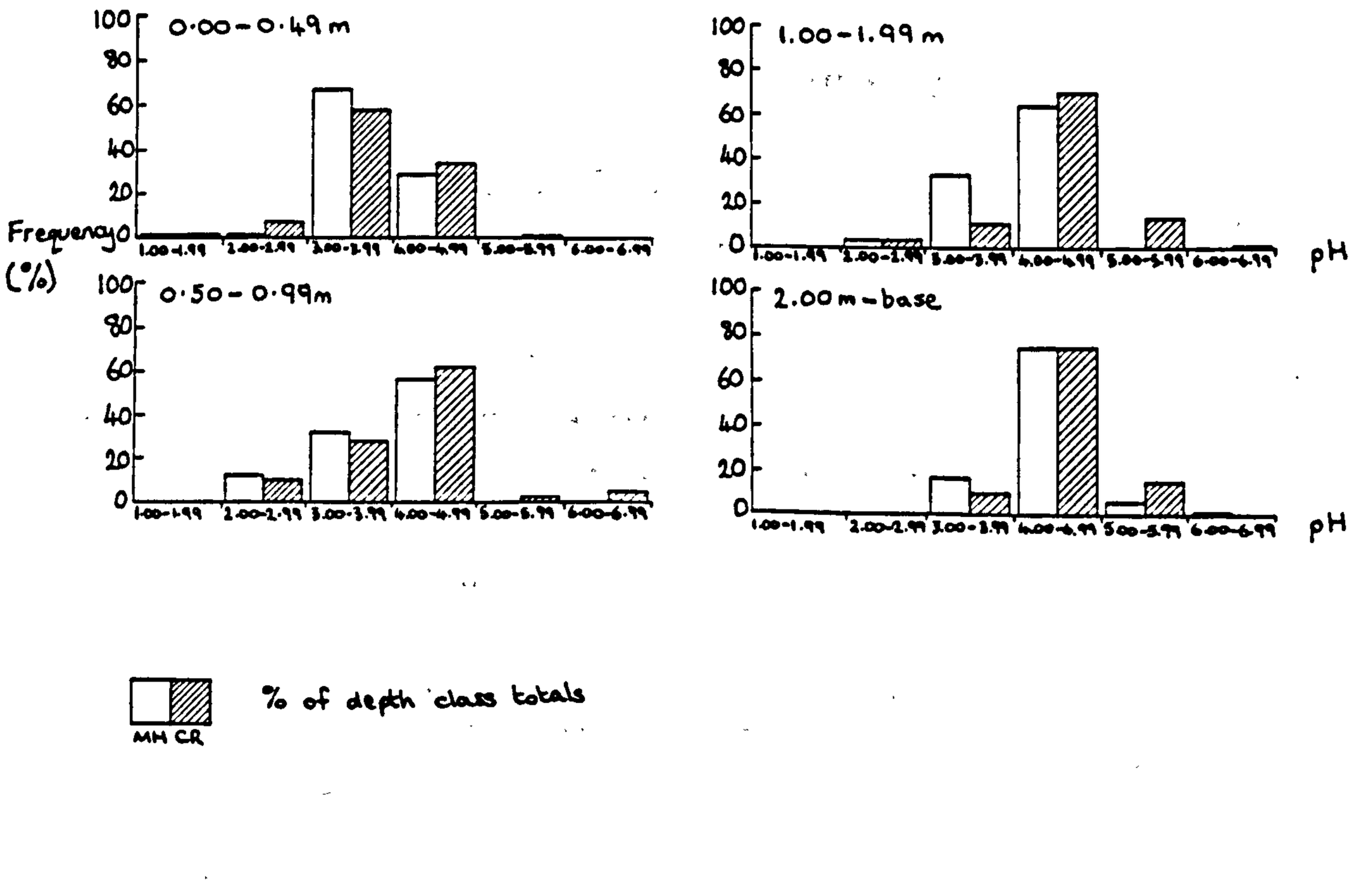
There was a decrease in pH over the top 50 cm, followed by a recovery over the next 50 cm, to -1 m. Below this the pH increased very gradually to the base. The shallow-peat changes were considerably larger at CR than at MH, decreasing from pH 4.3 to pH 2.6 over the top 50 cm in 1982, compared with a drop of only 0.6 units, from pH 4.1 to pH 3.5 over the same depth interval at MH. At both Sites, the 1983 pH values were less extreme, and, in general, slightly

FIG. 4.61 Seasonal changes in pH profiles at Moor House and Coom Rigg, 1982-1983. Mean values (1≤n≤20).



more acid, but the changes at CR were consistently bigger than at MH. The pH from -1 m downwards was between pH 3.9 and pH 4.4 at MH, and between pH 4.5 and pH 4.6 at CR. At the base of the profiles, irrespective of total peat depth, the mean variation in pH was very small, values lying between pH 4.3 and pH 4.6. Fig. 4.62 shows the increase in pH below -50 cm and the subsequent reduced rate of increase below about -150 cm at both MH and CR. The extreme pH values have clearly shifted upwards, by about two pH units at the lower end and one at the upper, towards a more basic range at -200 cm and below, compared with those in the top 50 cm.

FIG. 4.62 Change in frequency of individual classes of pH records, with depth



The analyses of variance to investigate the significance of the changes in pH with depth, were carried out on the same depth classes as for the seasonal analyses of variance. The results (Table 4.57), when compared with the seasonal significance levels in the Table, indicate that the changes in pH with depth are more pronounced than those which occur seasonally, and that although at least some seasonal

effect was seen down to about a metre, below which the effect was not significant, the change in pH at depths just greater than a metre were more significant, relative both to those of season at the same depths and to depth effects in the peat above and below. Over the entire peat profile (0-500 cm) the significance of seasonal pH changes was $p<0.05$, compared with $p<0.0001$ for changes with depth.

Fig. 4.61 includes plots of the seasonal components, which were combined to give the mean pH profiles. It is clear that the interaction of seasonal and depth effects produces a rather complex pattern of change in pH, about which it is difficult to generalise. The pH profile is not simply shifted one way or another as the season progresses, but its shape is distorted by the inconstant relationship of pH values and depth at different times of the year. The largest standard errors related to depths down to 1 m.

4.4.3 REDOX POTENTIAL PROFILES

All potentials referred to in this Section are reported relative to the hydrogen electrode (E_h). Potentials were recorded on all field visits between October 1981 and September 1983, with the exception of November 1981 and August 1982 at MH (Table 4.54, above). The data set thus represents all months of the year except January, February and November, with a distribution as shown in Table 4.58. The number of measurements made was as reported for pH, that is, between 5 and 9 on each block, and between 6 and 24 on each profile.

TABLE 4.58 Seasonal distribution of redox potential profiles recorded at Moor House and Coom Rigg.

	Jan		Feb		Mar		Apr		May		Jun		Jul		Aug		Sep		Oct		Nov		Dec	
	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P
MH	0	0	0	0	1	1	2	1	3	3	3	3	2	2	0	0	3	3	1	1	0	0	0	0
CR	0	0	0	0	0	0	3	2	3	2	4	4	2	2	2	2	3	3	1	1	0	0	2	2

B = number of blocks recorded (0 to -30 cm)
P = number of deep profiles recorded (-50 cm to base of peat)

Redox Potential

Fig. 4.63 summarises the distribution of the complete set of redox potential values at MH and CR, and allows a comparison of the general reduced state of the peat at the two Sites. The shape of the distribution is similar at MH and CR, and is somewhat asymmetrical, having respectively 65% and 75% of the records between 0-299 mV and the remaining records between 300-799 mV, at MH and CR (subtract 268 mV to give equivalent calomel electrode potential). From Fig. 4.63 there is no obvious difference in the overall redox potential at the two Sites.

FIG. 4.63 Redox potential of peat at Moor House and Coom Rigg

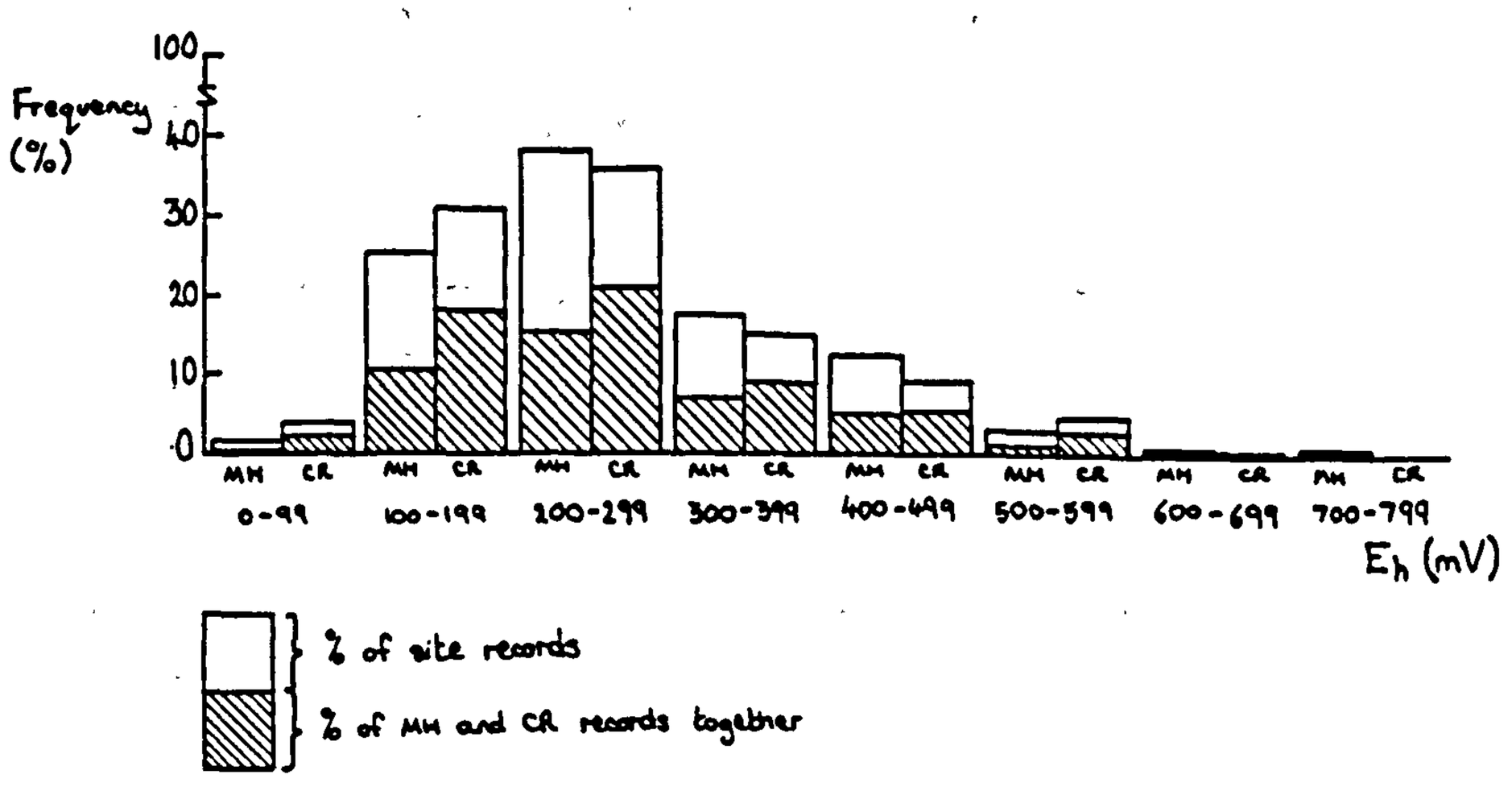
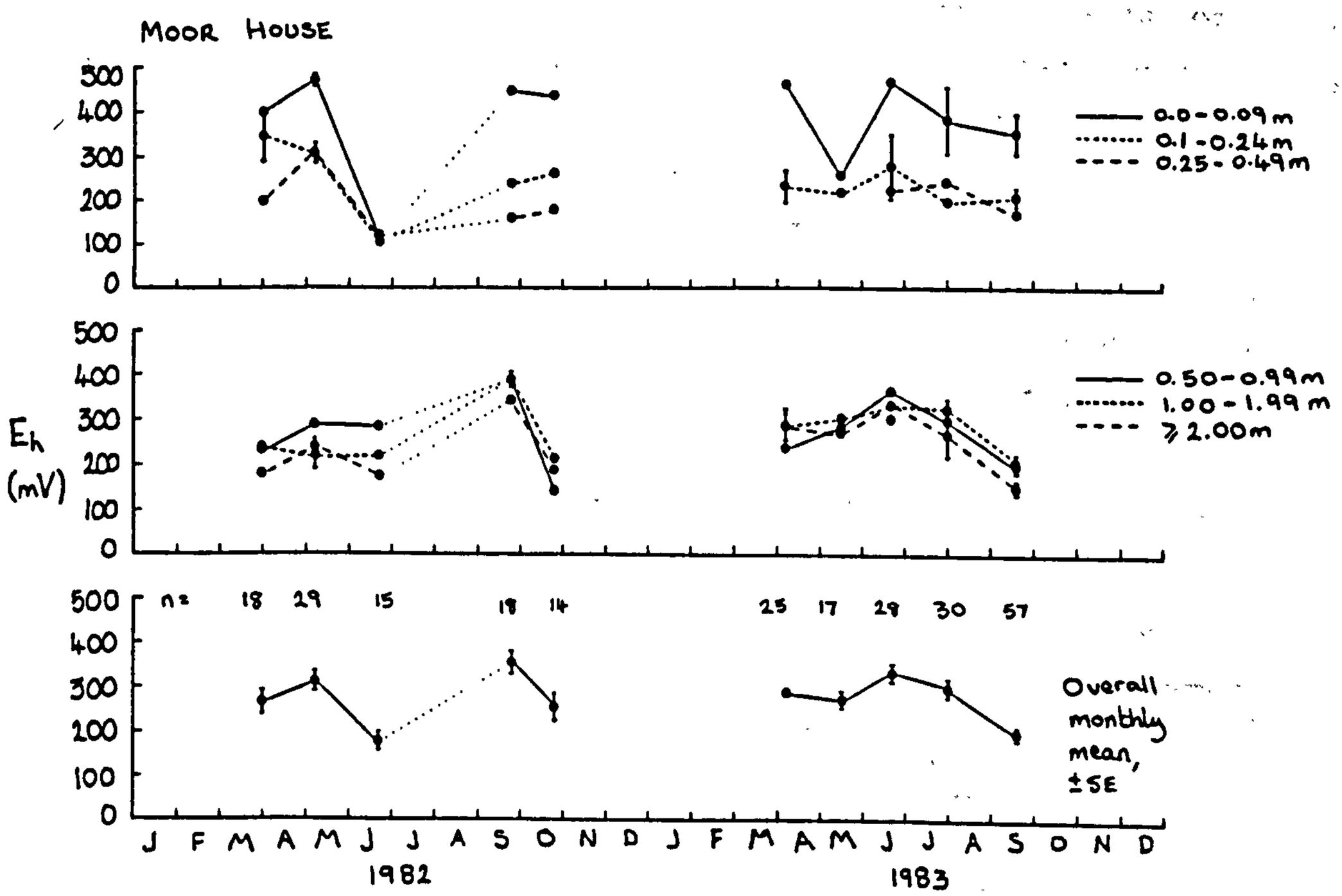


Fig. 4.64 illustrates the changes in redox potential at MH and CR over the two study seasons, taking the mean value for each month's records within the depth classes indicated.

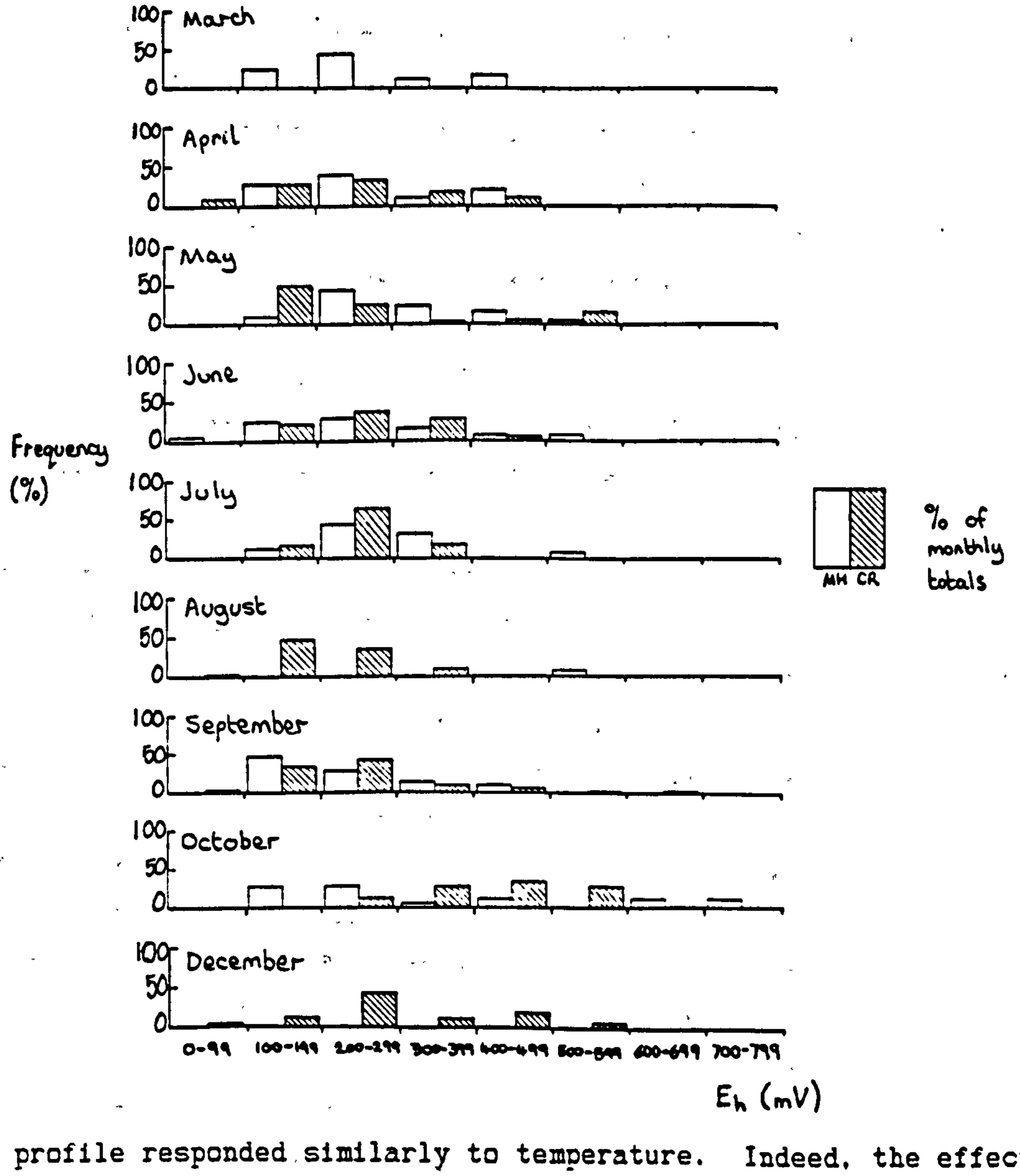
At both MH and CR there was a general decline in the redox potential from spring to late summer, followed by a recovery through autumn. The trends were similar in both years at both Sites, but there was variation in the timing and the size of the changes. The measured range of redox potential was considerably smaller in 1983 than in 1982 at both Sites.

FIG. 4.64 Seasonal changes in redox potential at Moor House and Coom Rigg, 1982-1983. Mean values (±SE where n>6) (2<n<22).



The distribution of data was wide (Fig. 4.65) so that the percentage frequency of data in each mV class was relatively low and absolute differences between classes were quite small. The scatter of data changed as the season progressed, suggesting that not all regions

FIG. 4.65 Seasonal change in frequency of individual classes of redox potential records



of the profile responded similarly to temperature. Indeed, the effect of depth is clear in Fig. 4.64. The range of potential in the top 10 cm was about 300-350 mV in 1982, compared with 245-300 mV between -10 cm and -24 cm, and 160-210 mV between -25 cm and -49 cm. The values were slightly different, but the trends were the same, in 1983. At any time, there was generally no more than 100 mV difference

between any two measured depths in a profile, below -50 cm, and the mean potentials for the season varied by less than 65 mV, compared with a difference of up to 200 mV difference between the top 10 cm of peat and that between -10 cm and -24 cm. The seasonal means at these shallow depths differed by roughly 100 mV.

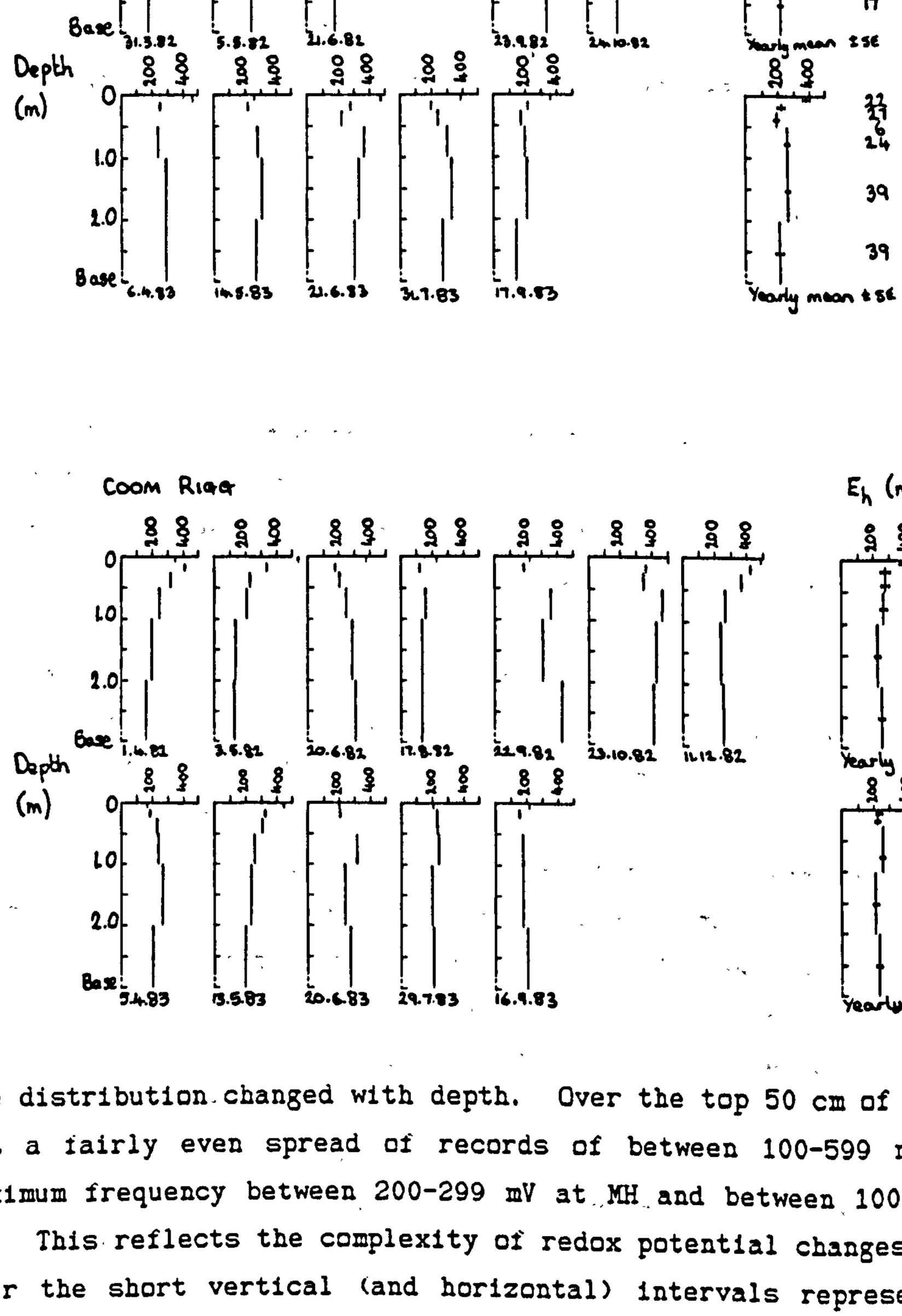
Despite the large standard errors for the mean potentials in the top 50 cm of peat, the seasonal changes were statistically significant. Standard errors were much smaller deeper in the peat.

Using MH and CR data together, analyses of variance were carried out, in parallel with those for the pH effects, to determine the significance of the seasonal changes in redox potential at different depths down the profile. All profiles, whether from the base up, or from the surface downwards, whether over the top 10 cm or the entire profile to the base of the peat, showed a highly significant seasonal pattern ($p<0.001$, Table 4.57). Such a seasonal effect, for example that seen between -200 cm and -500 cm, is not likely to be one resulting from temperature changes, and is in contrast to the seasonal pH results.

Fig. 4.66 shows the mean redox potential profile over each study season at MH and CR. The results for 1982 and 1983 at MH are remarkably similar, and indicate a maximum potential (390 mV) in the top 10 cm of peat, falling to a minimum (200-230 mV) between -25 cm and -50 cm, below which there was a slight increase again between -50 cm and -200 cm, before a small decrease to the base. At CR the maximum potential was also recorded at the surface (390 mV in 1982 and 220 mV in 1983), but the minimum (210-230 mV) occurred considerably deeper in the peat, between -100 cm and -200 cm in both years. Thus, apart from the 1983 maximum, the absolute potentials at MH and CR were similar, but the position of the minima were markedly different. The analyses of variance for the change in redox potential with depth (Table 4.57) returned highly significant results ($p<0.001$) for all depths of profiles from the surface downwards, but non-significant results for profiles from the base upwards, to 50 cm from the surface.

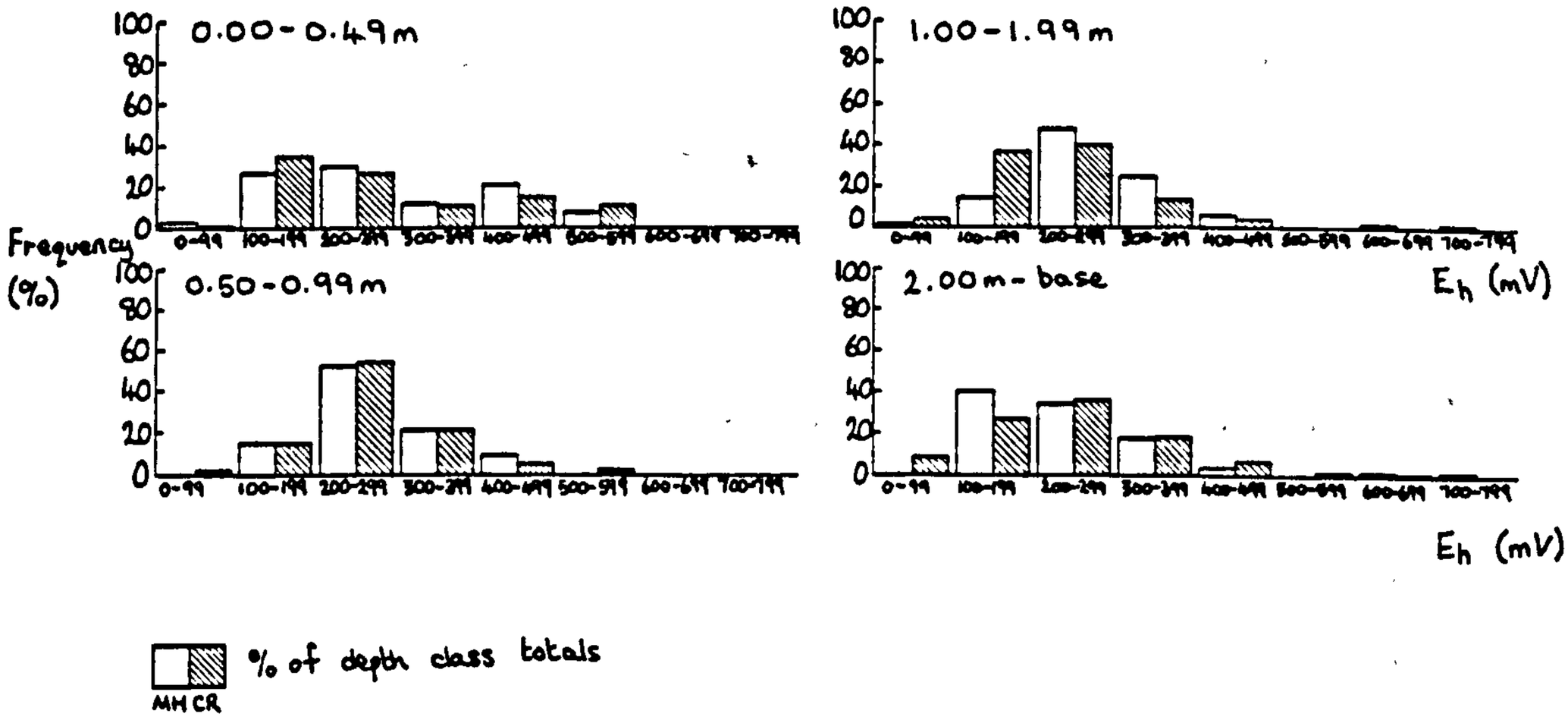
The range of potentials measured at different depths over the two years of the study is shown in Fig. 4.67. The shape and position of

FIG. 4.66 Seasonal changes in redox potential profiles at Moor House and Coom Rigg, 1982-1983. Mean values (±SE where n>6) (1<n<22)



the distribution changed with depth. Over the top 50 cm of peat there was a fairly even spread of records of between 100-599 mV, with a maximum frequency between 200-299 mV at MH and between 100-199 mV at CR. This reflects the complexity of redox potential changes occurring over the short vertical (and horizontal) intervals represented. In the 150 cm of peat below this, that is, between -0.50 and -2.00 m,

FIG. 4.67 Changes in frequency of individual classes of redox potential records, with depth



there was less scatter, with a clear maximum at both MH and CR in the 200-299 mV range. There was then a flattening of the distribution with depth. The increase in diversity towards the base of the peat may reflect an increased complexity of the total reduction-oxidation system with the supposed addition of mineral content.

As with pH, the mean redox potential profile masks seasonal changes, the complexity of which can be seen in Fig. 4.66. The position of the maxima and minima on the profile shift. At MH in 1982 the minimum appeared to occur at shallower depths as the air temperature increased, and drop back down again in the autumn, but in 1983 the minimum was consistently recorded between -10 cm and -40 cm. At CR in 1982 there was also a tendency for the minimum potential to move up the peat profile with an increase in temperature and drop back in October and December. As at MH, there was no clear pattern of movement in 1983. On five occasions, once at MH and four times at CR, the shallow-peat profile of redox potentials was convex, that is, the surface potential was more reduced than that in the peat below. This was always seen either at the beginning of the season, or at the

warmest times of year; when oxygen demand might be expected to be greatest.

4.4.4 SULPHIDE CONCENTRATION PROFILES

VARIATION WITH DEPTH AND SEASON

'Sulphide concentration' throughout this section refers to total sulphide concentration. Records were made on all field visits between October 1981 and September 1983, with the exception of August 1982 (Table 4.54), and represent all months of the year except January, February and August. The monthly distribution of the data is shown in Table 4.59. The number of measurements made was as for pH and redox potential.

TABLE 4.59 Seasonal distribution of sulphide profiles recorded at Moor House and Coom Rigg.

	Jan		Feb		Mar		Apr		May		Jun		Jul		Aug		Sep		Oct		Nov		Dec	
	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P	B	P
MH	0	0	0	0	1	1	2	1	3	1	3	3	2	2	0	0	3	3	1	2	0	0	0	0
CR	0	0	0	0	0	0	2	2	3	2	2	2	2	2	0	0	3	3	1	1	0	1	2	2

B = number of blocks recorded (0 to -30 cm)
P = number of deep profiles recorded (-50 cm to base of peat)

Fig. 4.68 shows the range of sulphide concentrations encountered during the study period. The sulphide concentration classes are given in pS units (pS = $-\log[S^{z-}]$, where $[S^{z-}]$ is reported in mol dm^{-3}. This is equivalent to using pH units to describe H^+ ion concentration). The units may be readily interconverted using the conversion bar in Fig. 4.68 or the factors given in Table 4.60.

By far the highest frequency of records, 48% at MH and 67% at CR, fell within the range 0.32-32 ppm S^{z-} (pS 4.99-3.00). Of MH records, 3.5% were at or above the range of the electrode sensitivity (≤pS 0.00, according to the Ag/S electrode manual) and at CR 1%. Respectively, 12% and 10.5% were apparently below it (that is,

≥pS 7.00). A saturated sulphide solution has a concentration of about 0.1 mol dm^{-3} S^{2-}, or 3.2 x 10^{3} ppm. From Fig. 4.68 it is clear that less than 2% of all records were made on fully saturated solutions.

FIG. 4.68 Total sulphide concentration in peat at Moor House and Coom Rigg

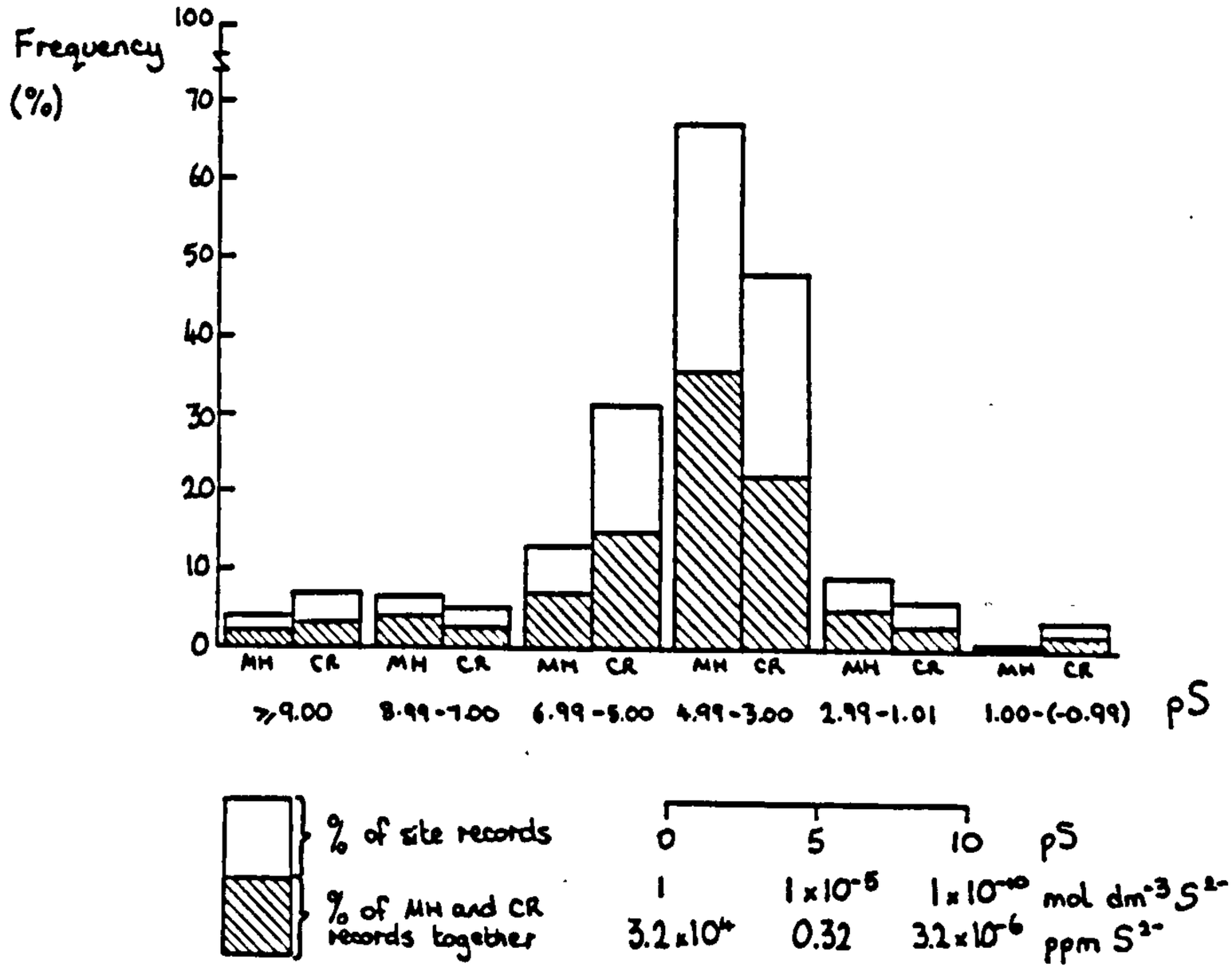
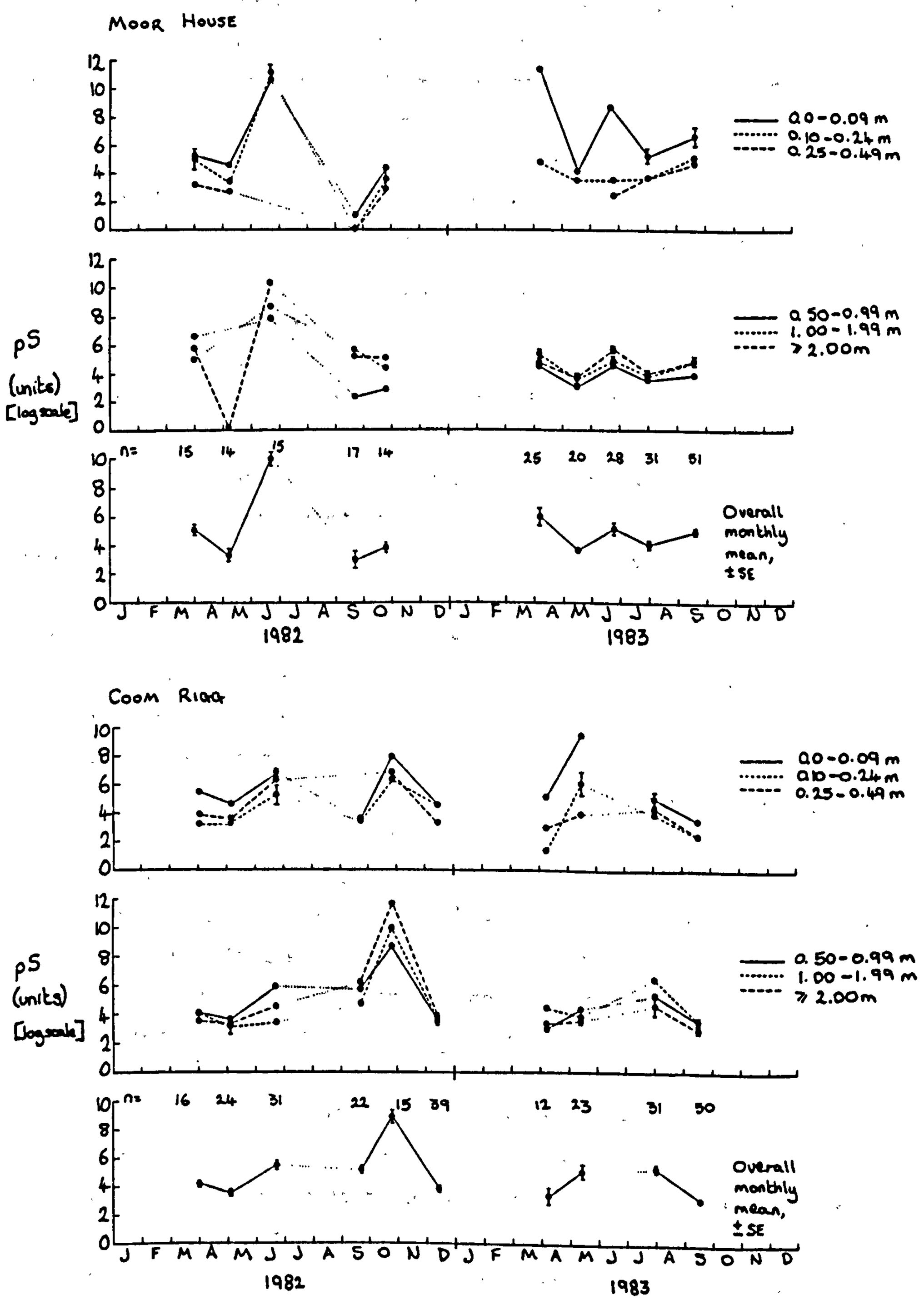


TABLE 4.60 Conversion factors for sulphide concentration units.

S^{2-} concentration		
mol dm^{-3}	ppm	pS
10	3.2 x 10^{5}	-1.00
1	3.2 x 10^{4}	0.00 ←
0.1	3.2 x 10^{3}	1.00
0.01	3.2 x 10^{2}	2.00
1 x 10^{-3}	32	3.00
3.2 x 10^{-5}	1	4.49
1 x 10^{-5}	3.2 x 10^{-1}	5.00
1 x 10^{-7}	3.2 x 10^{-3}	7.00
1 x 10^{-9}	3.2 x 10^{-5}	9.00 ←

0.1 mol dm^{-3} represents roughly a saturated sulphide solution (≈pH4)
← limits of sensitivity of Ag/S electrode, as given in manual (10^{0} mol dm^{-3} and 10^{-7} mol dm^{-3} S^{2-})

FIG. 4.69 Seasonal changes in total sulphide concentration at Moor House and Coom Rigg, 1982-1983. Mean values (±SE where n≥6) (1≤n≤20).



In general, CR data showed slightly higher concentrations of sulphide than did those of MH.

The mean of each month's data for MH and CR within the depth classes shown is illustrated in Fig. 4.69. The sulphide concentration varied widely over the seasons, with a tendency to increase in the warmer months. However, there was much variation in the absolute concentration and the extent of the changes between Sites and between seasons, and results were more consistent between depths at any one Site than between Sites or seasons. The mean seasonal range in sulphide concentration was biggest at MH, being 6.4 ppm in 1983 and 10.1 ppm in 1982.

In Fig. 4.70 the percentage frequency histograms for the sulphide concentration classes are plotted separately for each month. There is considerable change in sulphide concentration range and distribution over the year, significant changes apparently occurring between monthly field visits, and not consistently in any direction.

Fig. 4.71 (p.300) illustrates the monthly changes in sulphide concentration at different depths in the profile, and it is evident from the Figure that the sulphide concentrations at any two depths do not bear a constant relationship to one another. On most visits, the minimum sulphide concentration was recorded at the surface, but on a number of occasions it was found below a metre, and with no apparent consistent relationship with season. Absolute concentrations varied by up to 6.6 pS units within a single profile and by even more between profiles, and there was no consistent profile shape within a Site or a clear seasonal pattern of change. Standard errors were largest in the shallower peat; sometimes calculated as 10% or more of the mean. When MH and CR 1982 and 1983 data were clumped together, the patterns were still complex, but some general trends were suggested: in all recorded months except March, the sulphide concentration increased over the top 25 cm of peat; in October, the minimum mean sulphide concentration was recorded at 2 m and deeper, whereas in May, June and July the minima were found in the top 10 cm of peat; conversely, the maxima tended to occur nearer the surface in the cooler months and deeper down at warmer (air temperature) times of the year. The highest concentrations over a field season were recorded at between -25 and

FIG. 4.70 Seasonal change in frequency of individual classes of total sulphide concentration records

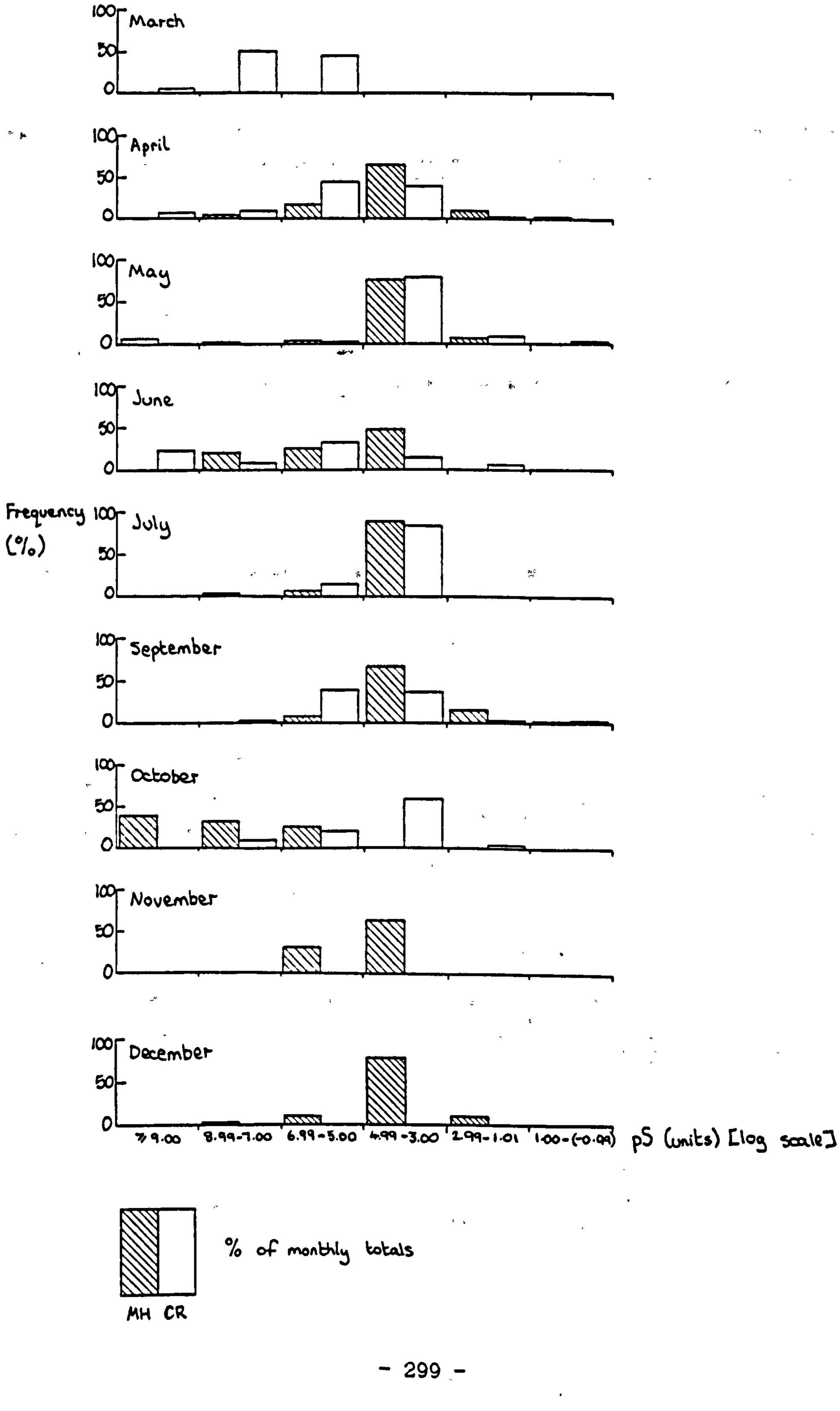
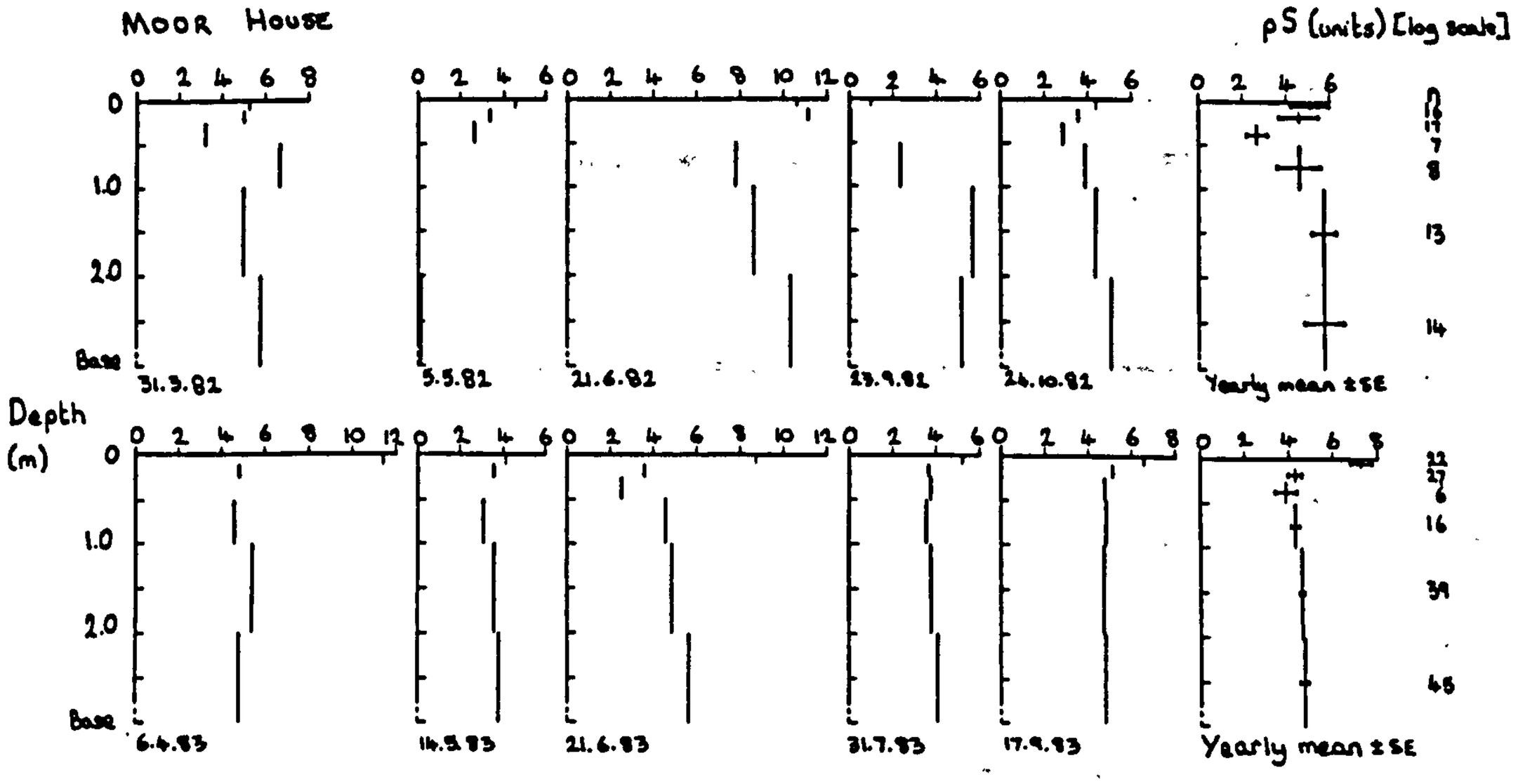
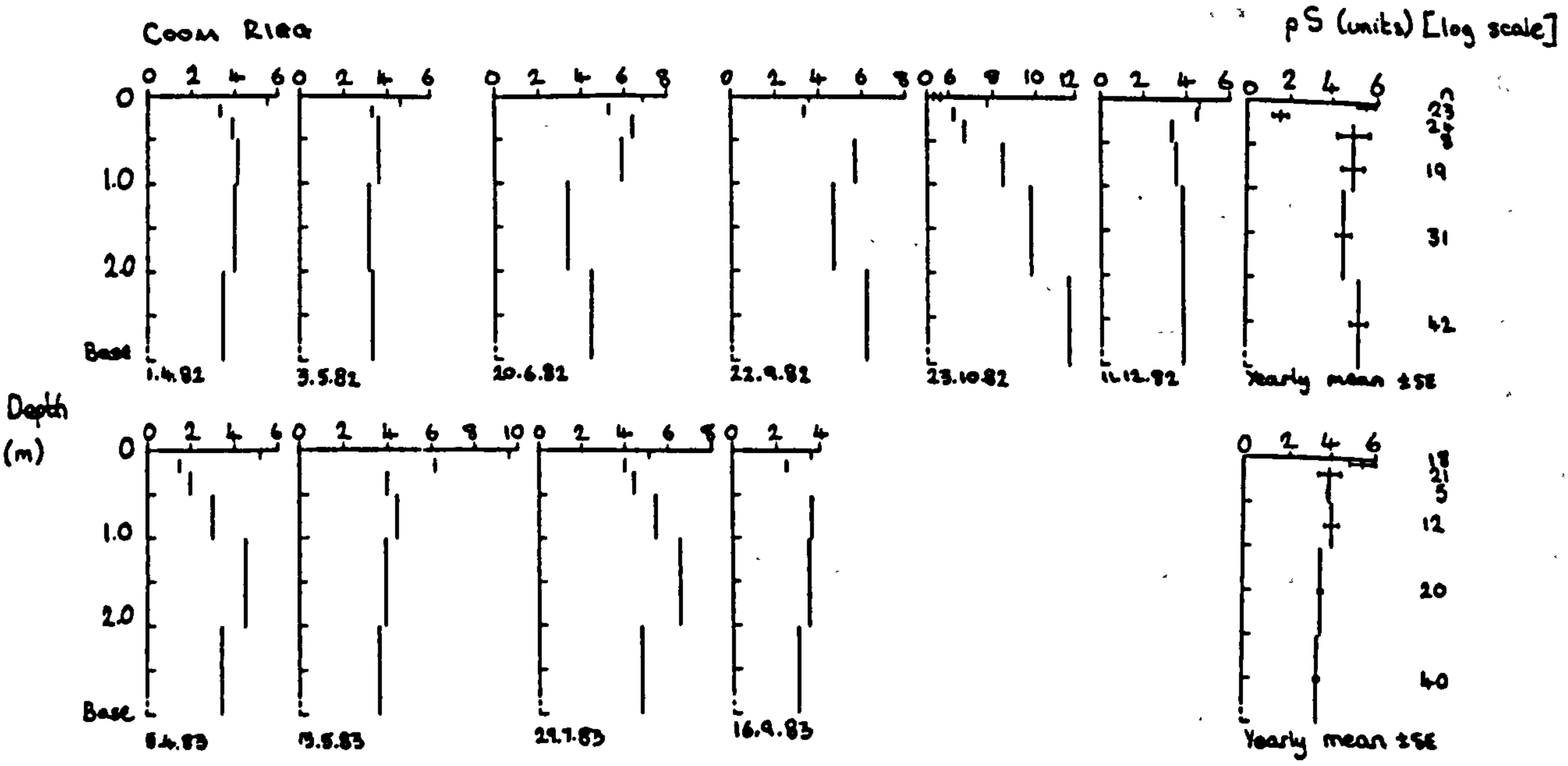


FIG. 4.71 Seasonal changes in pS profiles, Coom Rigg, 1982-1983. Mean values (±SE where n>6) (1<n<20).





-50 cm, with minima between -50 cm and -1 m. All data considered together, the maximum sulphide concentration at depths greater than -50 cm coincided with that at -25 to -50 cm, but occurred a month later than at -10 to -20 cm.

For the seasonal changes in the top 10 cm of peat, the analysis of variance returned a non-significant result (Table 4.57), but when data for 10-15 cm were included in the analysis the result was significant ($p<0.05$) and this increased to the $p<0.01$ level for the 0-20 cm profile, suggesting that seasonal differences are greatest over a narrow band of the profile between -10 and -20 cm. Including the 20-25 cm interval in the analysis did not increase the significance level further, but profiles of 0-50 cm and 0-100 cm gave $p<0.001$. As for redox potential, and in contrast to pH, the seasonal effect on sulphide concentration was apparently highly significant ($p<0.001$) at the base of the peat and in all profiles tested from the base up to 50 cm from the surface.

Considering the combined MH and CR data set, in the top 10-20 cm of peat the minimum sulphide concentration (1760 ppm, pS 3.3) occurred in June, compared with the corresponding maximum redox potential of 315 mV, in May, and the maximum concentration (6820 ppm, pS 0.7) lagged about a month behind the minimum redox potential of 115 mV, in August. At depths of 1 m and more the maximum sulphide concentration (2620 ppm, pS 1.2) and a minimum in the redox potential (206 mV) coincided (in May), as, conversely, did the minimum sulphide concentration (0.1 ppm, pS 5.6) and maximum redox potential (326 mV) in October.

The results of the analyses of variance for redox potential (Table 4.57) were similar to those of sulphide concentration, except that changes in potential in the top 10 cm of peat were highly significant, but those of sulphide concentration were not. Below -20 cm the results were very similar, and in contrast to those of pH. The monthly redox potential and sulphide concentration profiles illustrated in Figs. 4.66 and 4.71 are remarkably similar in form, particularly at MH, and in view of the considerable variability of each parameter considered alone.

RELATIVE IMPORTANCE OF SELECTED FACTORS CONNECTED WITH TOTAL SULPHIDE CONCENTRATION

It is clear from the preceding sections that total sulphide concentration, pH and redox potential in the peat change with depth, and that the shape of the profiles changes also with season, and although the sulphide concentration and redox potential profile changes appear to correlate well in general, detailed differences do occur. Any rôle of pH is even less clear from a comparison of the profiles. The sulphide concentration profile is the result of an integrated response to a number of factors, of which only those most likely to be of much importance have been measured here. In order to try and clarify the relationship between total sulphide concentration, pH, redox potential and temperature at different depths in the peat, a multiple regression approach was used. At the pH of the peat in which the measurements have been made, practically all the sulphide is present as H_2S (Appendix F). At pH 5.00, 99% of the total sulphide is in the form of H_2S, the proportion dropping to 91% at pH 6.00. Of the 582 pH records made, 34 (5.8%) were at or above pH 5.00 (6 at MH (1.0%) and 28 at CR (4.8%)), and only 6 (1.0%) at or above pH 6.00 (1 at MH (0.2%) and 5 at CR (0.9%)). Hence, it was considered acceptable to equate total sulphide concentration with concentration of H_2S present in the peat at the time of measurement. The multiple

TABLE 4.61 Variables used in multiple regression analyses of total sulphide concentration.

Variables

y pS (units) (dependent)
x_1 Depth (negative values, cm)
x_2 Air temperature (+1.5 m) at the time of the record (°C)
x_3 Median peat-air interface temperature (+5 cm) for period since previous field visit (°C)
x_4 Predicted peat temperature at depth and time of record, calculated from sine wave equation based on MH data collected during the present study, viz:
$T_{(z,t)} = 4.8 + 16.0\, e^{-z/40.0} \sin((2\pi t/365.0) - z/40.0)$ (°C)
x_5 Predicted peat temperature at depth and time of record, calculated from sine wave equation based on 1981 Met. Off. data, viz:
$T_{(z,t)} = 4.9 + 7.5\, e^{-z/80.0} \sin((2\pi t/365.0) - z/80.0)$ (°C)
x_6 E_h (mV)
x_7 pH (units)

Sulphide Concentration

regression analyses were carried out using total sulphide concentration (pS units) as the dependent variable. The independent variables entered into the regressions are given in Table 4.61. The correlation table for the individual variables is shown in Table 4.62. The correlation coefficients are based on MH and CR data, together.

TABLE 4.62 Correlation table for total sulphide concentration and selected peat characteristics. A full description of variables and units is given in Table 4.61.

		y	x_1	x_2	x_3	x_4	x_5	x_6	x_7
y	pS	1.00	-0.13	0.05	0.28	0.02	0.01	0.41	0.16
x_1	Depth		1.00	-0.04	-0.15	0.07	0.10	-0.17	0.46
x_2	Air temp. (+1.5 m)			1.00	-0.06	-0.05	-0.04	0.02	0.05
x_3	Interface temp. (+5 cm)				1.00	0.16	0.15	0.22	0.20
x_4	Peat temp. (MH) (Predicted)					1.00	-	0.02	0.03
x_5	Peat temp. (Met. Off.) (Predicted)						1.00	0.04	0.05
x_6	E_h							1.00	-0.17
x_7	pH								1.00

As expected, the most closely-correlated variable with total sulphide concentration (≡ concentration of H_2S) was the redox potential, r=0.41, indicating a reduction in sulphide concentration with increased oxidation state of the peat. The median interface temperature since the previous field visit gave the next highest correlation coefficient, 0.28, indicating a decrease in sulphide concentrations with increasing temperature. The only other variables to account for more than 10% of the variation were pH (r=0.16) and depth (r=-0.13). Thus, pH is apparently correlated with the absolute sulphide concentration, as well as playing a rôle in determining the proportion of the total which is present as H_2, HS^- and H^{2-}, that is, the position of the sulphide solution equilibrium. No other temperature variables were connected with sulphide concentration.

Sub-sets of the complete data, in addition to the entire data set itself, were subjected to (linear) multiple regression analyses to determine whether, and if so what, changes occurred in the factors of most importance in influencing the sulphide concentration at different depths in the peat. Two analyses were carried out on each data set; firstly using the peat temperatures predicted from the MH study data (i.e. using dependent variables x_2 - x_5 and x_7 - x_8), and secondly

using those based on the MH Met. Off. data (i.e. variables x_2 - x_4 and x_5 - x_8). Table 4.63 summarises the results of the analyses. The regression equation involving all the significant ($p<0.05$) variables for each analysis is given in Appendix O.

TABLE 4.63 Summary of results from multiple regression analyses of factors affecting total sulphide concentration in field peat. Significance level shown where $p<0.05$. Empty cells represent a significance level of $p>0.05$. A dash (-) indicates a variable not included in the analysis. Regression estimates given in Appendix O. A full description of the variables, with units, is given in Table 4.61.

Analysis no.	Data set analysed	Significance level of variable						
		Depth	Temperature				E_h	pH
			Air	Interface	Peat (MH)	Peat (Met.Off.)		
		x_1	x_2	x_3	x_4	x_5	x_6	x_7
1a	MH&CR (MH)			0.001		-	0.0001	
1b	MH&CR (Met. Off.)			0.001	-		0.0001	
2a	MH (MH)		0.038	0.018	0.006	-	0.001	0.008
2b	MH (Met. Off.)		0.047	0.015	-	0.003	0.0001	0.003
3a	CR (MH)		0.001	0.001		-	0.0001	0.040
3b	CR (Met. Off.)		0.001	0.001	-		0.0001	0.040
4a	MH&CR <10 cm (MH)	0.047		0.030		-	0.014	
4b	MH&CR <10 cm (Met. Off.)	0.047		0.030	-		0.014	
5a	MH&CR <15 cm (MH)	0.005		0.017		-	0.007	
5b	MH&CR <15 cm (Met. Off.)	0.005		0.017	-		0.007	
6a	MH&CR <20 cm (MH)	0.001		0.011		-	0.005	
6c	MH&CR <20 cm (Met. Off.)	0.001		0.011	-		0.005	
7	MH >150 cm (MH)		0.001			-	0.0001	
8	MH&CR >150 cm (MH)	0.031				-	0.0001	
9	MH >250 cm (Met. Off.)	0.041			-	0.033	0.001	0.005
10	MH&CR >250 cm (Met. Off.)			0.005	-		0.0001	

It is clear from Table 4.63 that both sets of predicted peat temperatures gave very similar results; indeed, only in the analysis of the complete MH data set (analysis no. 2), was there any difference at all between the significance of the variables in the pair of analyses. In both these cases the predicted peat temperatures were highly significant, over the whole profile, coming second only to redox potential.

Whilst all the regression equations were highly significant ($p<0.001$), it is important to note that the highest r^2 value was 0.37

(for the complete MH data set and involving all variables except depth). The lowest r^2 value was 0.18, for the analysis of MH data from peat at -250 cm or more (analysis no. 10). These low r^2 values indicate that the relationships between sulphide concentration and the variables tested here, although real, are not described by a simple linear expression.

Without exception, the redox potential was by far the most important influence on the sulphide concentration, its significance ranging from $p<0.014$ in the top 10 cm of peat (MH and CR data together; analysis no. 4), to $p<0.0001$ for almost all the remaining data sets. When the complete MH and CR data set was analysed (analysis no. 1), the only significant ($p<0.05$) variables were found to be redox potential ($p<0.0001$) and the median interface temperature since the previous field visit ($p<0.001$). When MH and CR data were separated (analyses 2 and 3, respectively), both Sites showed the sulphide concentration to be influenced by the redox potential, interface temperature, air temperature and pH, with redox potential the most important ($p<0.001$), but the relative importance of the remaining factors differed.

Analyses 4-6 were carried out on data representing the top 10, 15 and 20 cm of peat (MH and CR together), respectively. The significance level of the redox potential was still the highest of all the variables, but was much increased compared to the other analyses on deep peat. There was a marked increase in the importance of redox potential between the top 10 cm of peat ($p<0.014$) and the top 15 cm of peat ($p<0.007$), but far less difference when data for the next 5 cm of the profile, 15-20 cm, were included ($p<0.005$). In the top 10 cm of peat the general interface temperature was the second most important factor after the redox potential ($p<0.03$), and the (integral) factor, depth, showed a significance level of $p<0.047$. Over the next 10 cm of the profile, to 20 cm, the influence of both these variables increased, giving $p<0.011$ for the interface temperature and $p<0.001$ for the depth. Thus, even over the top 20 cm of peat the relative importance of the three significant variables changed: over the 0-10 cm profile they increased in significance in the order depth, interface temperature, redox potential; whilst over the 0-15 cm and

0-20 cm profiles their significance increased in the order interface temperature, depth, redox potential. 'Depth' represents a summary term for all contributory factors and is not, therefore, directly comparable with any one of the other variables included in the analyses. But the change in the order of importance of this and, particularly, of the interface temperature over just a few centimetres illustrates how complex any description of the sulphide concentration profile in terms of measured variables is likely to be.

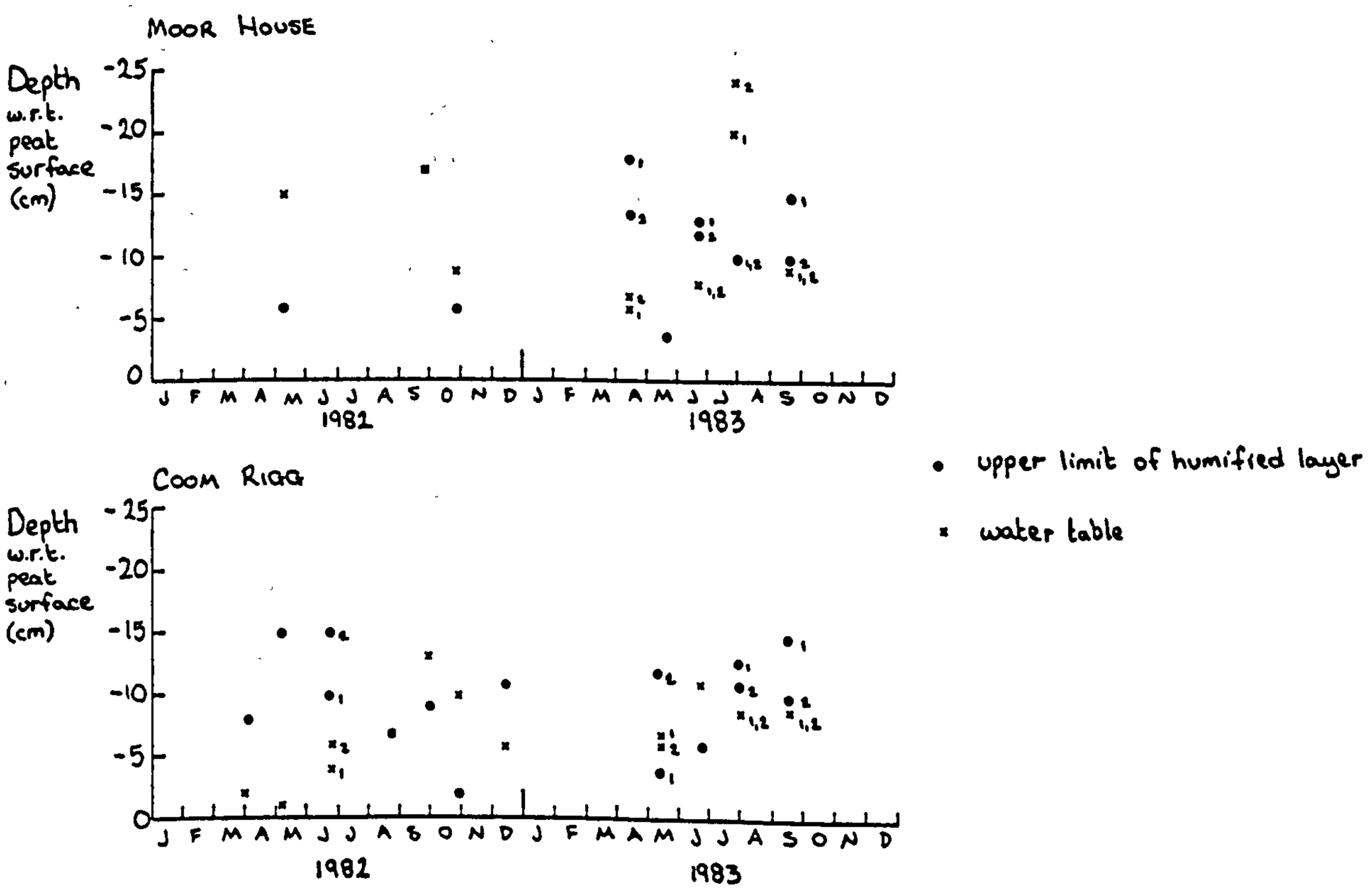
Analyses 4-6 were designed to determine from what factors the sulphide concentration could be predicted near the top of the peat profile where daily and annual temperature cycles were significant. In contrast to this, analyses 7-10 used data from depths in the peat where, according to the predicted temperatures, daily and annual cycles did not occur (Fig. G.9, p.461). Thus, data from -150 cm and below were used with the MH data predicted temperatures (analyses 7 and 8), and from -250 cm and below with the Met. Off. data predicted temperatures (analyses 9 and 10). The results varied, with all variables being significant in one or more of the four analyses, but redox was most important in every case, followed by either pH, peat or surface temperature, depending on the data set used.

It is worth re-emphasising the low r^2 values for the regressions at this point. It is clear from the multiple regression results that redox potential is the most important factor connected with the sulphide concentration and the median interface temperature also gives, consistently, significant results except in the deepest regions of the peat profile. The complexity of the relationships between the independent variables and the sulphide concentration is also apparent, and Table 4.63 shows the general shift in importance of a number of factors at different depths, and in some cases over only a few centimetres, of peat. However, the linear analyses completed here are even then over-simplifications, as the low r^2 values of the regression equations illustrate, and the description of the absolute relationship between the significant factors and the sulphide concentration in these peats is likely only to be approached by a more detailed, polynomial, treatment.

RELATIONSHIP BETWEEN TOTAL SULPHIDE CONCENTRATION, WATER LEVEL AND DEGREE OF HUMIFICATION

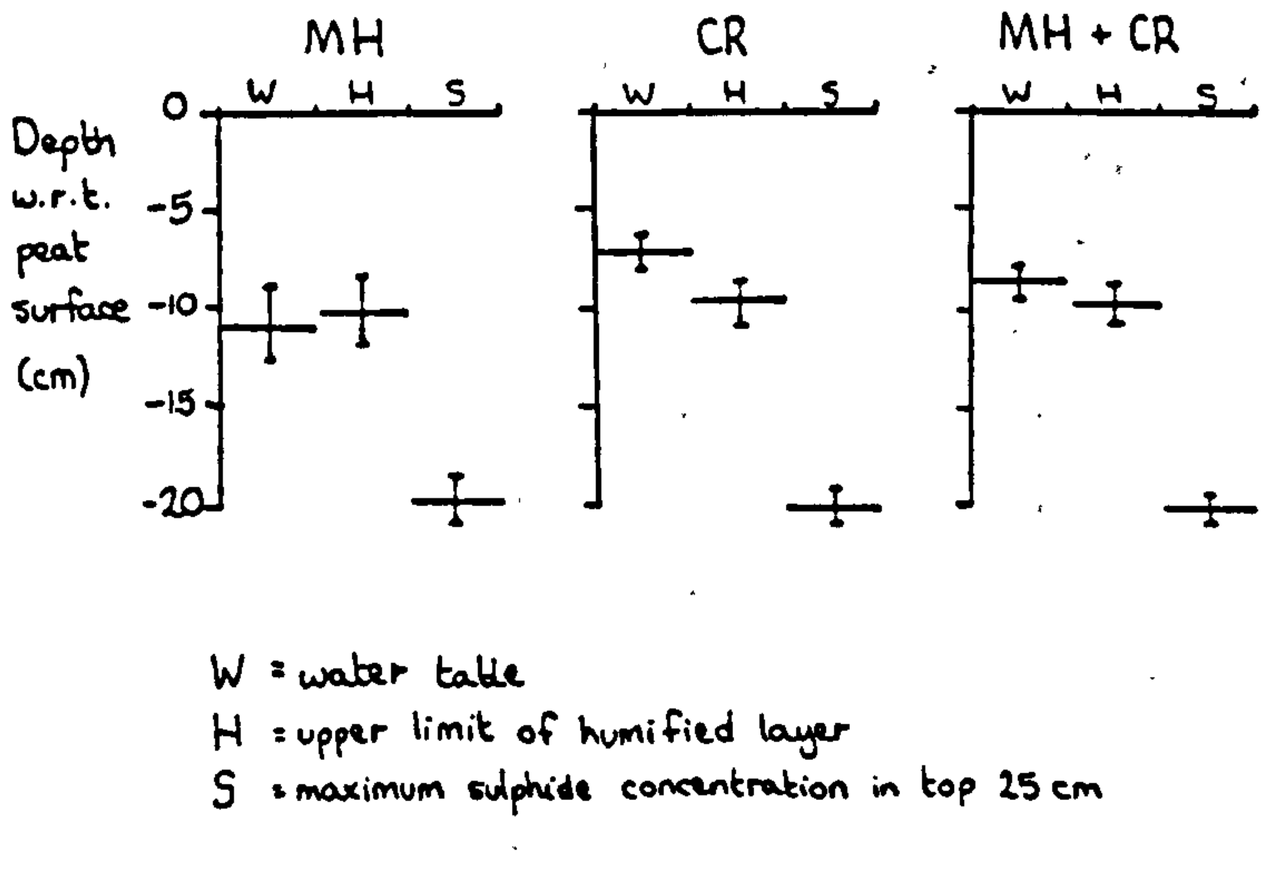
When the surface blocks of peat had been removed for pH, redox and sulphide measurements to be made, the water level and the depth of the upper limit of the humified layer were recorded, and these somewhat limited data (n=27) have been examined for any consistent relationship between sulphide concentration and either water level, depth of the humified layer, or both. Since the upper limit of the humified layer lies approximately at the mean minimum summer water table depth (Clymo 1984, citing Ivanov 1981), it would not be expected to bear a constant relationship to water level measurements made over almost an annual range of depth. The range of recorded water levels at the profile sites was 0 cm to -24 cm at MH, and from -1 cm to -13 cm at CR. The corresponding depths of the onset of humification were -4 cm and -10 cm at MH, and -9 cm and ≈ -15 cm at CR. From the very limited observations available, there was no clear seasonal

FIG. 4.72 Seasonal variation in the depths of the water table and humified layer



relationship between the water table and humified layer depths at MH or CR (Fig. 4.72). The mean depth of the water level and of the upper limit of the humified layer, and the mean depth at which the maximum sulphide concentration occurred in the top 25 cm are given in Fig. 4.73. The data showed much variation in all three variables.

FIG. 4.73 Position of mean water level, humified layer and maximum sulphide concentration in the top 25 cm of peat. Mean of records from peat blocks used for pH, E_h and S^{2-} measurements, March 1982-September 1983, ±SE.



However, it was clear that the maximum sulphide concentration in the top 25 cm occurred at about 10 cm below the upper limit of the humified layer. The variation in the latter reflects the differences at each of the coring sites used. The variation in the water level data is also partly attributable to this, but includes seasonal variation. Hence, the depth of the maximum sulphide concentration could not so accurately be described relative to the water level.

The relationship between sulphide concentration, water level and humification is complex; the present data revealed no consistent quantifiable differences in depth of the variables measured, and no apparent seasonal trends. Such a limited data set is insufficient to elucidate the complex changes in absolute and relative behaviour of these peat characteristics, and no further analysis has therefore been attempted.

4.4.5 MOVEMENT OF SULPHIDE ZONE UPPER LIMIT

INTRODUCTION

As described in Section 3.1.4 (Qualitative Sulphide Record), records of the 'sulphide zone' in the top 30 cm of peat were made in the garden minibog M1, in selected, representative, garden cores and at selected sampling sites at MH and CR. Silver-plated brass strips were placed in the peat at approximately monthly intervals in the garden and on each visit to the field, and were left in place for two days. During this time the silver became discoloured due to the deposition on its surface of Ag_2S, when the concentration of (total) sulphide ions was greater than 10^{-5} mol dm^{-3} (0.32 ppm) (Section 3.1.4, Qualitative Sulphide Record). 'Sulphide zone' is therefore taken to mean the region of peat in which the total S^{2-} concentration was high enough to give discolouration of the strips. Records were made from April 1981 to December 1983 in M1 and from February 1981 to December 1983 in the garden cores. At MH records were kept between May and October 1982 and between May and September 1983, and at CR between May and December 1982 and April and September 1983.

INTERPRETATION OF THE DISCOLOURED SILVERED STRIPS

The pattern and colours which developed on the strips were complex. It was hoped to be able to interpret these colours quantitatively, but attempts to 'calibrate' the discolouration proved unsuccessful (Section 3.1.4, Qualitative Sulphide Record). The strips were used, therefore, to give qualitative information about the depth at which the sulphide zone begins in the peat.

There was an element of subjectivity in choosing the criterion on which to base the measurement of the depth of the sulphide zone upper limit. There was not always a clear-cut horizontal boundary between discoloured and pristine silver. In many cases there was such a boundary, but in others any of the following possibilities could occur (usually only one):

i) the very edge of the strip could be discoloured for up to 10 cm above such a boundary,

ii) a strip might show an occasional small, irregular patch with intensely discoloured, thin, margins and a pristine silver centre (interpreted as gas bubble outlines),

iii) the boundary might be clear-cut, but sloped such that the intersection of the boundary with the edges of a strip occurred over a vertical distance of up to 5 cm,

iv) a strip might show no discolouration immediately below the peat or water level, but discolouration deeper down and again immediately above the air-peat or air-water interface.

In the presentation of the results which follows, the 'depth of the sulphide zone' indicates the depth (upper limit) at which discolouration was continuous, horizontally, for at least half the 1.25 cm-wide strips; it does not imply a narrow horizontal band of discolouration at that depth, but a continuous sulphide zone from that depth down at least as far as the strip reached. The strips were 30 cm long, and almost without exception they were discoloured along the rest of their length from the point of first discolouration, as defined here.

After looking at many strips it was clear that the idea of a 'sulphide zone' was not fallacious; there were certainly significant concentrations of sulphide present and these persisted down the peat core, but the onset of the zone was gradual in some cases. The method of measurement chosen was easy to adopt, and the numerical results reflected faithfully the subjective differences in the extent of the discolouration.

The discolouration which was seen occasionally above the air-peat or air-water interface was interpreted to be the result of a drop in the water level or, more likely, the effect from H_2S vapour above a concentrated solution.

Within the sulphide zone, as can be seen from Fig. 3.5 (p.81 and inside back cover), discolouration was complex. The colour variation was blotchy, and there were no clear trends in intensity or hue. Given the failure in the laboratory to calibrate the discolouration for known sulphide concentrations, no further attempt was made to

interpret it on strips exposed to peat. The following account deals with the movement of the upper limit of the sulphide zone.

EFFECT OF TEMPERATURE ON SULPHIDE ZONE DEPTH

The complete sulphide zone record for M1, P1, L1 and H1 is shown in Fig. 4.74. The results for M1 can be considered to show 'natural' fluctuations, since water level was not regulated. Theoretically, the complication of a fluctuating water level should be absent from the plots for P1, L1 and H1, but it is clear that the water level was less constant than had been hoped for. Nonetheless, the large fluctuations seen in the M1 water levels are less extreme and more gradual in the cores, so any effect of water level changes has been successfully reduced.

Fig. 4.74 shows clearly movement in the upper limit of the sulphide zone over the year and that some of the changes may be associated with seasonal temperature changes, though it is apparent that water level is also involved. The seasonal changes are most clear in the M1 plot, where the sulphide zone drops deeper below the peat surface (to a maximum of around -20 cm to -25 cm) in the winter months, reaching up to the surface again in early summer. In the three experimental peat cores there is also a drop in the sulphide zone over the autumn and into winter, but it is less extreme.

Fig. 4.75 shows the corresponding field sulphide zone results for the 12 sampling sites where records were made over the two seasons. Air and peat temperatures are shown for comparison.

Changes in the field sulphide zone were complex, apparently more so than in M1, although seasonal trends were apparent. The three MH microhabitats varied in this respect. The seasonal movements in the sulphide zone were not absolutely consistent between seasons, but triplicate buckets representing each of the three microhabitats (9 in all) showed similar changes. With the exception of pools in 1982, most buckets at MH indicated an increase in the sulphide zone in the autumn, rather than a drop as was seen in the garden peat. At CR the autumn drop occurred, but here, in 1982, the sulphide zone also fell in the summer months. Of the three microhabitats, the sulphide zone

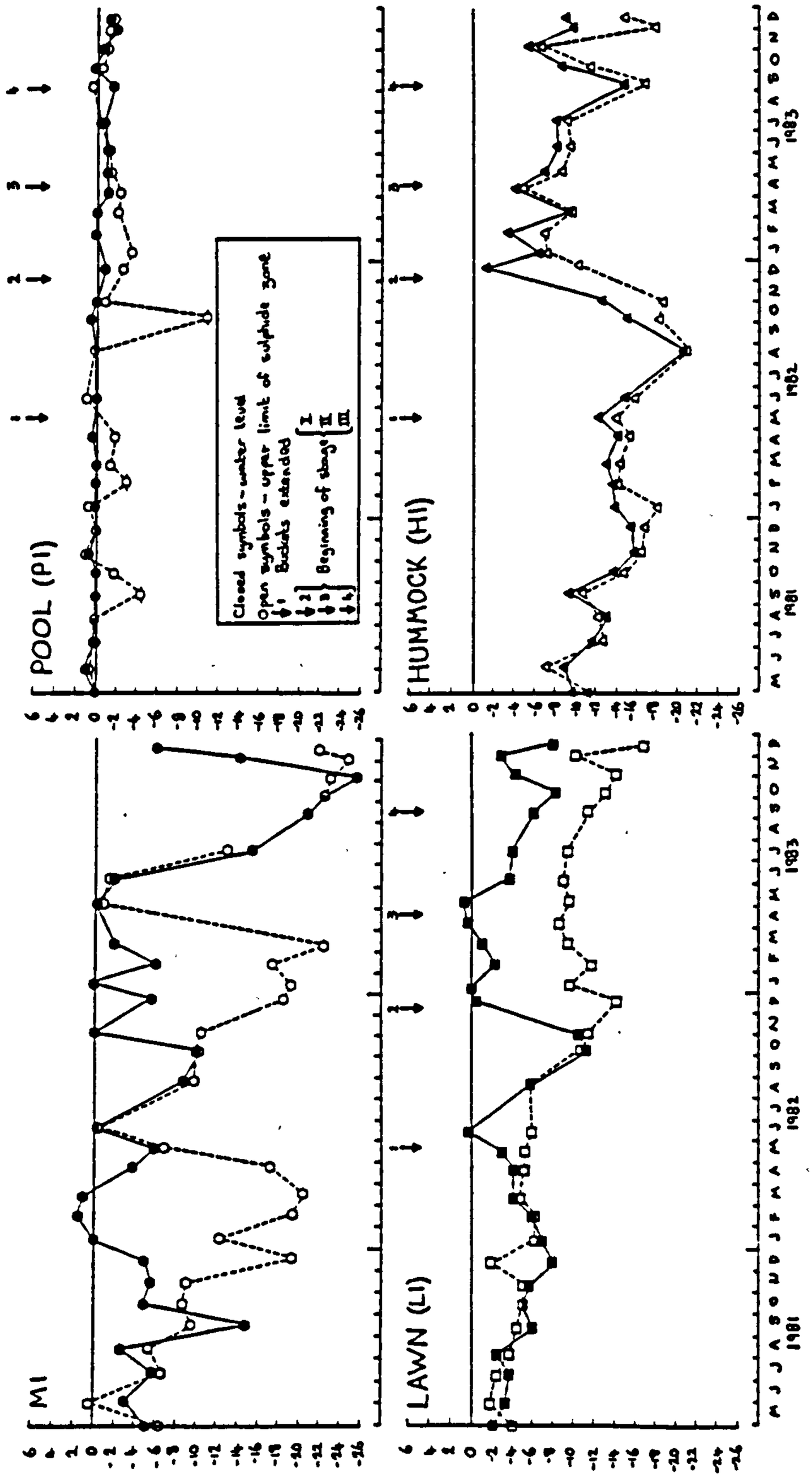
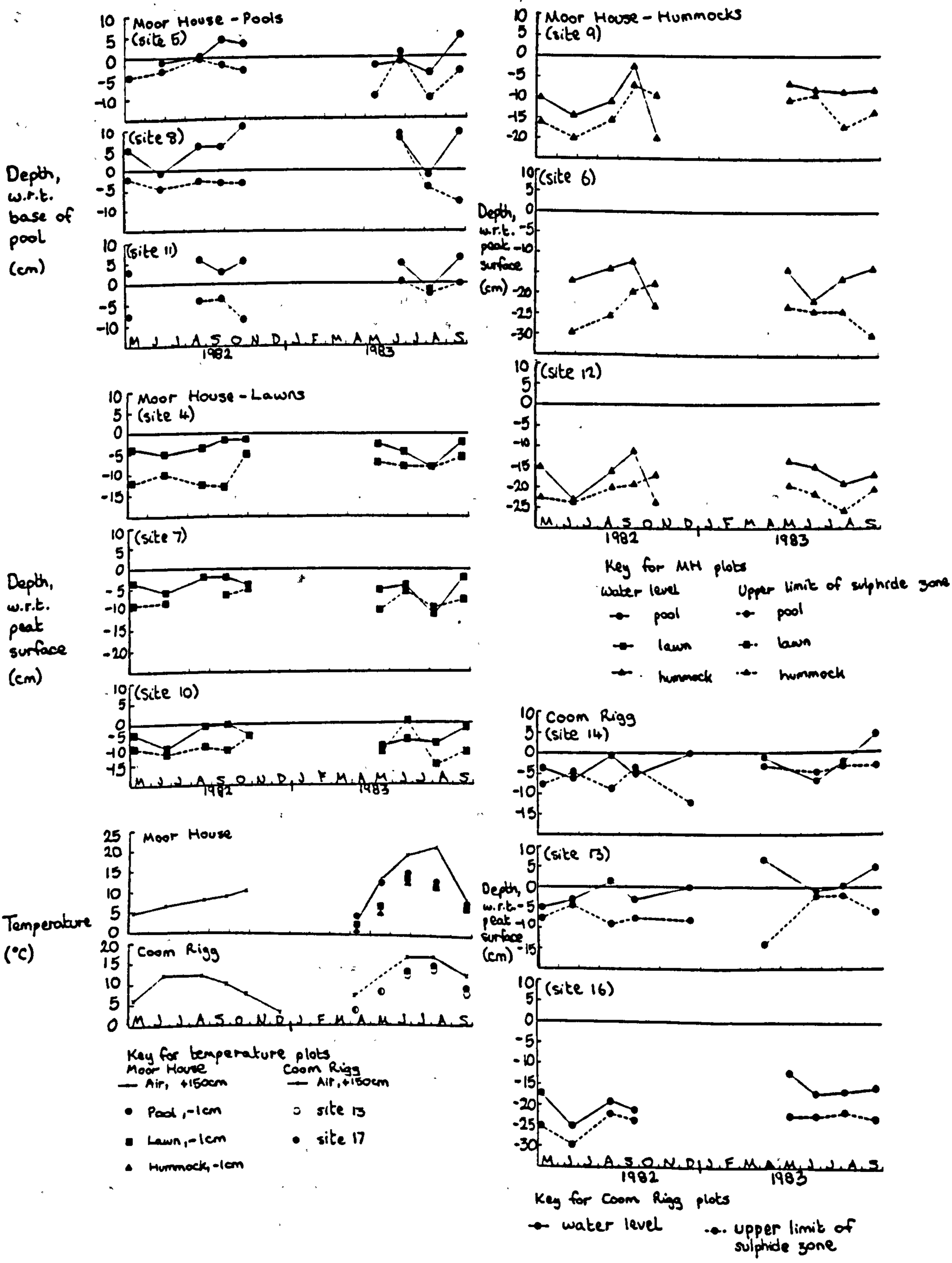


FIG. 4.74 Changes in the depth of the sulphide zone upper limit in the Garden peat, 1981-1983

FIG. 4.75 Changes in the depth of the sulphide zone upper limit at selected sampling sites, 1982-1983



in the hummocks showed the most consistent seasonal trend, at least in 1982, the zone rising gradually from May to June to reach nearest the surface in either September or October; thus the cycle was shifted relative to that in the garden. The sulphide zone in pools fluctuated over only about 5 cm during the season compared with a range of about 10-15 cm in hummocks.

To try and clarify any association between temperature and sulphide zone depth, and whether the association is seasonal or applies differentially to the three microhabitats, or both, (linear) correlation coefficients were calculated.

TABLE 4.64 Description of water level and temperature variables used in field sulphide zone correlation and regression analyses.

Label	Name	Description
x_1	WLEV	Depth of the water level, below peat surface (measured) (cm)
x_2	AIRREC	Air temperature (+1.5 m) at time of removal of silvered strip (measured) (°C)
x_3	MED2D	Median 'interface' temperature (+ 5 cm) (½(max. + min.)) over the two days that the silvered strip was left in the peat (measured) (°C)
x_4	MEDLAST	Median 'interface' temperature (+ 5cm) (½(max. + min.)) for the period since the previous sulphide zone record (measured) (°C)
x_5	MH30REC	Predicted temperature at -30 cm at the time of removal of the silvered strip, based on the sine wave equation using data available from the present study (see Appendix G) (°C)
x_6	MH30MED	Mean predicted temperature at -30 cm for the period since the previous sulphide zone record, based on the sine wave equation, using data available from the present study (see x_5, above) (°C)
x_7	MET30REC	Predicted temperature at -30 cm at the time of removal of the silvered strip, based on the sine wave equation, using 1981 Met. Off. data (See Appendix G) (°C)
x_8	MET30MED	Mean predicted temperature at -30 cm for the period since the previous sulphide zone record, based on the sine wave equation, using 1981 Met. Off. data (see x_7, above) (°C)

The temperature variables investigated are described in Table 4.64. Variables x_1 to x_4 were measured during the study, the remaining four were predicted using the sine wave equation described in Appendix G. The appendix describes the difficulties encountered during the estimation of the peat damping depth, and the present temperature predictions were carried out using two different estimates of damping depth and the corresponding temperature parameters on which these were based. Values for the predicted

temperature variables x_5 and x_6 were based on the sine wave equation incorporating data collected during the present study, whereas the values for variables x_7 and x_8 were obtained using the same equation but substituting 1981 MH Met. Off. data. For further details, see Appendix G. In both cases the only variable in the predictions was the date (position in the annual cycle); the remaining variables in the equation were assigned the values given in Figs. G.9b and c, p.461, for the MH (field peat) and Met. Off. equations, respectively.

The values of variables x_3 and x_4, involving the calculation of the median temperature at +5 cm using the maximum and minimum temperatures, were only available for the period June to September 1983, after installation of the maximum and minimum thermometers. Hence all regression analyses involving MED2D or MEDLAST were based on a limited data set representing a maximum of 36 records made on the three field visits during that period, compared to the complete data set consisting of 111 records, which could be used to investigate the importance of the remaining six variables (including water level). Not only are the MED2D and MEDLAST variable sets limited in size relative to the others, but they also represent a limited period of the year. This is reflected in the mean and range of the temperatures recorded (and predicted), as shown in Table 4.65. The restricted data sets have higher mean temperatures and narrower temperature ranges than the full sets.

TABLE 4.65 Mean and range of temperatures represented by full and restricted data sets.

Variable		Full (n=11)		Restricted (n=36)	
		Mean (°C)	Range (°C)	Mean (°C)	Range (°C)
x_2	AIRREC	11.2	3.0-22.0	16.0	9.00-22.00
x_3	MED2D	-	-	13.5	7.25-22.25
x_4	MEDLAST	-	-	14.8	2.75-21.25
x_5	MH30REC	6.5	-0.3-12.3	10.9	9.70-12.30
x_6	MH30MED	6.2	-1.9-12.0	10.1	7.30-12.00
x_7	MET30REC	6.6	0.8- 9.9	8.6	7.40- 9.90
x_8	MET30MED	6.3	1.5- 9.9	9.1	8.20- 9.90

The (linear) correlation coefficients, r, for the association of the individual temperature variables and the depth of the sulphide

zone are shown in Appendix Pa for both full and restricted data sets. The data have been analysed for MH and CR separately, and for each of the three microhabitats at MH, in addition to an analysis of all the data together.

The most obvious result to be seen from the coefficients is that pool and lawn sulphide zone depth was more closely associated with temperature than was that in hummocks, when temperatures were relatively high (restricted data set). In most cases the association was negative.

A closer examination of the correlation coefficients in Appendix Pa reveals the complexity of any relationship between the position of the sulphide zone and air or peat temperature; even the results from the restricted data set do not lend themselves to generalisations. Many of the results were apparently inconsistent; some of the associations were positive, others negative, and different temperature variables were important depending on the data set being analysed (Sites and microhabitats). None of the measured data temperature variables returned coefficients higher than 0.60; the individual microhabitat results were highest: MHP gave r=-0.50 for MEDLAST and r=0.61 for MED2D, and the corresponding values for MHL were -0.59 and 0.38.

The predicted temperatures (restricted data set) gave higher coefficients than had the corresponding measured surface temperatures. Again, the closest association was seen in pools and lawns (r=-0.51 to -0.72); that for all the data together was very low (r<-0.17).

When the analyses were repeated on the full data set, in general, peat temperature was more important than that of air. There was less difference between microhabitats in the importance of temperature.

The analysis of the temperature effect on the position of the sulphide zone was repeated with sub-sets of the entire data set representing temperatures during the times when each temperature variable in turn was above and below the annual mean field temperature of 5°C. In this suite of analyses the full data set was used (i.e. non-restricted), and regressions were carried out on all sub-sets of the data containing seven or more corresponding items for all variables. The resulting correlation coefficients are shown in

Appendix Pa. Only a small proportion of the data related to times when the determinant temperature variable was less than 5°C. However, some direct comparisons were possible.

The majority of the correlation coefficients for the association of the sulphide zone depth with temperature were negative, and most were very low, the maximum value in all the analyses aimed at comparing 'warm period' and 'cold period' data sets was -0.51. The effect of most of the temperature variables was apparently reduced during warmer periods, and although part of this is probably due to the larger data set involved, some changes appeared too large to be attributable to this cause alone, and in some instances the correlation coefficient increased.

EFFECT OF THE WATER LEVEL ON SULPHIDE ZONE DEPTH

a) Long-term

It is clear from Figs. 4.74 and 4.75 that water level is an important factor associated with the depth of the sulphide zone upper limit in peat. In most cases the sulphide zone began a few centimetres below the water level, but the vertical distance between the two was not constant over the year. Hence, pools, lawns and hummocks in the garden and in the field showed different mean water levels and different mean sulphide levels, over the study period.

It is convenient to consider first of all the results from M1, as representative of the 'natural' changes in both water level and sulphide zone depth. The relationship between the two is clearly seasonal. Dividing the data into two groups defined by air

TABLE 4.66 Seasonal variation in relative depths (cm) of water level and sulphide zone in garden (M1) peat. Seasonal mean values (±SE 1980-1983) and (n).

		Year to Oct 1981	Year to Oct 1982	Year to Oct 1983	1980-83
<10 °C	Water level	-	-1.9 (6)	-2.6 (5)	-2.2 ±0.9 (11)
(Nov-Apr)	S^{2-}	-	-16.2 (6)	-17.5 (5)	-16.8 ±1.4 (11)
≥10 °C	Water level	-3.8 (5)	-6.3 (4)	-12.1 (5)	-7.5 ±2.0 (14)
(May-Oct)	S^{2-}	-5.5 (5)	-6.4 (4)	-9.1 (4)	-6.9 ±1.8 (13)

temperature <10°C and >10°C (roughly the garden annual mean temperature) gave May to October as one seasonal group and November to April as the second. Table 4.66 shows the mean water level and sulphide zone depths for each 'season' in M1. The difference in the distance between the water level and sulphide zone depth at different times of the year is clear; the drop in sulphide zone relative to the water level in the cool period was significant at the $p<0.001$ level, but there was no significant difference between the two between May and October (Wilcoxon signed-rank test). The pattern may be explained if temperatures are considered and it is assumed that a microbial population capable of producing the sulphide is present in the peat at least up to the water level. Then, while peat temperature is high, microbial sulphide production may be assumed to keep pace with its loss from the peat, so maintaining a sufficiently high concentration to register on the silvered strips. When the peat cools down, however, microbial activity will decrease; the 'hole' is assumed to be the result of diffusion out while the rate of production is low.

Turning now to the microhabitat differences in the garden peat, all three peat cores showed a fluctuating water level and sulphide zone depth, relative to the peat surface. On analysis certain trends were suggested by the data.

Table 4.67 summarises the differences in water level for each stage of the experiment, and gives the depth of the sulphide zone in each of the three cores relative to the water levels. It should be remembered that the stages are confounded with the time of year. This was unavoidable.

The significance of the differences in the water levels between microhabitats at each stage of the garden experiment was tested using the Wilcoxon signed-rank test. P1, L1 and H1 all showed significant differences ($p<0.01$) from each other at each stage. There were sufficient data only to be able to test M1 against the other microhabitats during the Pre I stage, and the results were significant ($p<0.01$) except between M1 and L1, suggesting that the minibog water régime, although not regulated, behaved similarly to that of L1, when the median water levels were considered. This is reflected in the mean Pre I water levels for L1 (-4.0 cm) and M1 (-3.5 cm).

Sulphide Zone

TABLE 4.67 Summary of water level and sulphide zone depth changes during garden experimental period.

Date	Stage of exp^{t}	Peat core	P1			L1			H1		
21/05/81-	PRE I	Water level	0,9	±0,3	30	-4,0	±1,0	30	-9,9	±0,4	30
04/11/82		Sulphide zone	-1,6	±0,9	14	-0,2	±0,7	16	-1,3	±1,1	17
20/12/82-	I	Water level	-1,3	±0,2	15	-2,8	±0,2	15	-9,2	±0,3	15
14/04/83		Sulphide zone	-1,8	1,2/-3,3	5	-11,0	-8,4/-13,7	5	-3,9	-0,3/-7,5	5
28/04/83-	II	Water level	-7,9	±0,6	13	-4,5	±0,5	13	-10,4	±0,2	13
11/09/83		Sulphide zone	-0,5	-0,1/-0,8	3	-5,7	-0,9/-10,4	3	-1,5	-1,1/-1,8	3
26/09/83-	III	Water level	-9,5	±1,0	8	-4,0	±0,2	8	-10,9	±0,3	8
14/12/83		Sulphide zone	0,7	2,1/-0,7	5	-7,7	-4,8/-10,6	5	-3,9	-1,4/-8,3	5

- Upper limit of sulphide zone (cm) relative to water level
- Water level depths (cm) relative to the peat surface, except for P1 where the water levels are the same as the peat surface and the negative value reported here refers to this level relative to the bucket rim, to indicate how the peat 'expands' as the water level is increased and 'contracts' as it is decreased
- where n<5 the median depth, range (highest level/lowest level) and n are given
- where n>5, the mean depth ±SE and n are given

There were insufficient data to be able to test the sulphide zone depth behaviour in the same way. Taking the data for sulphide zone relative to the peat surface together for all stages for each microhabitat in turn, an analysis of variance showed that for this, too, there was a significant difference ($p<0.001$) between the microhabitats. Taking the same data for the Pre I stage only gave a similar result. The relationship between sulphide zone and water level depth was investigated. The results of applying the Mann-Whitney U test to determine the significance of the distance between the two levels between microhabitats are summarised in Table 4.68. There were sufficient data for only Pre I stage analysis ($14 \leq n \leq 17$).

We would expect, if the depth of the sulphide zone in the peat were solely dependent on the depth of the water level at any particular time, and if the relationship between the two were constant for all microhabitats, that comparing the depth of the sulphide zone relative to the water level between microhabitats would give no significantly different results. Significant differences do not

TABLE 4.68 Comparison between P1, L1 and H1 PRE I stage sulphide zone levels. Data tested were the sulphide zone depths relative to the water table, for each microhabitat, during the PRE I stage of the garden experiment.

	P1	L1	H1
P1	-	ns	ns
L1		-	**
H1			-

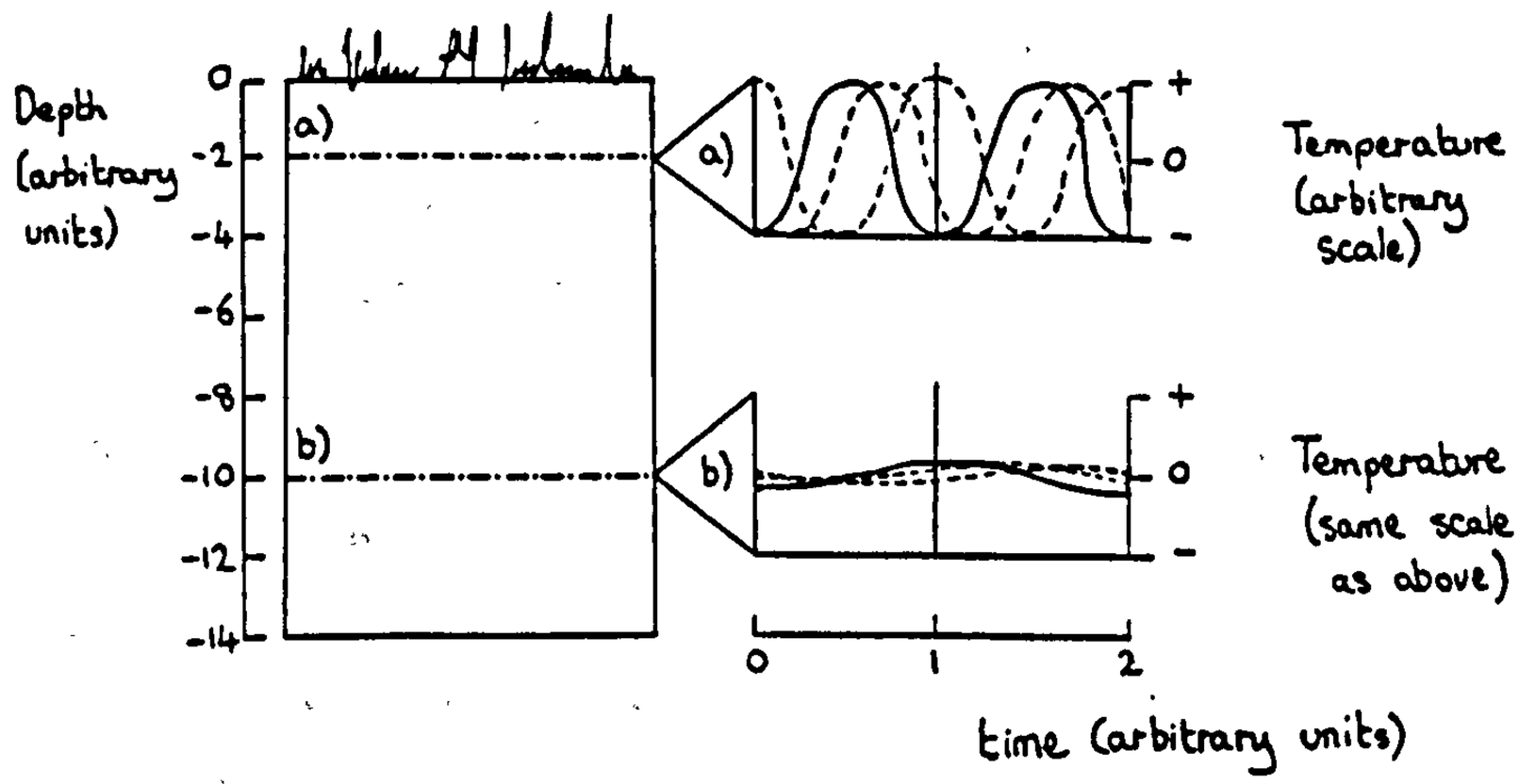
ns no significant difference
- no comparison

indicate that there is no relationship, but that such a relationship may not be constant, or is an over-simplification; that is, the sulphide zone depth is not only dependent on the simultaneous water level. However, non-significant results do lend weight to the idea that the sulphide zone fluctuations are related to those of the water level and are not random.

In view of the possibility that in some cases there may be a relationship between sulphide zone and water level which can be expressed simply, the complete data set for each microhabitat in turn was tested for a linear regression between these two variables (sulphide zone here relative to the peat surface). From Fig. 4.74 this does not appear totally unlikely. In the event, only H1 gave a regression coefficient suggesting such a relationship (r=0.86), the coefficients for P1, L1 and M1 were 0.03, 0.01 and 0.15, respectively, when testing all the data together. From Table 4.67 it is evident that the water level in H1 was much lower than in the other (controlled) cores and may explain this result. In the peat, the further a point is from the surface, the smaller the amplitude and the longer the wavelength of temperature fluctuations. If the zone of potential activity of the micro-organisms responsible for producing the sulphide in the peat is regulated by the water table, but their rate of activity is more closely related to temperature, then the relationship of water table to activity (i.e. the sulphide zone depth) will approximate more closely to linear as changes in temperature are reduced. The more constant the temperature the more constant the activity at any given depth, all other things being equal. For

example, micro-organisms present in peat which has a constant water table less than about 3 cm from the surface could be subject to diurnal temperature fluctuations of, typically, about 10°C. Hence their activity will fluctuate significantly over a 24-h period. In

FIG. 4.76 A possible effect of temperature on the relationship between water level and sulphide zone



contrast, micro-organisms living in peat which has a constant water level at about 10 cm depth will experience smaller and slower temperature fluctuations, as those at the surface become damped. The slower rate gives longer periods of relatively constant temperature conditions and hence the microbial activity is more constantly related to the water level than at the surface. These two contrasting situations are illustrated schematically in Fig. 4.76 If this is the case, we would not expect a strong linear relationship between sulphide zone and water level close to the surface. This hypothesis is supported by the results of a linear regression analysis between sulphide zone depth and water level (both relative to the peat surface) carried out on the data of the Pre I stage only, for each microhabitat. Compared with the complete data sets the values of the correlation coefficient, r, increased for P1 and L1 from 0.03 to 0.41 and from 0.10 to 0.58, respectively, remained the same for H1 (0.86 to 0.85) and changed from 0.38 to -0.23 for M1. Referring to Fig. 4.74 the explanation would seem to be that, for L1, after the Pre I stage

the water level increased but the sulphide zone did not move up with it, possibly prevented by the lower temperatures at that time of year. The negative value of the correlation coefficient for M1 clearly reflects the relative behaviour of the water level and sulphide zone there.

Fig. 4.75, above, illustrates the depth of the upper limit of the sulphide zone and the water level in the nine buckets recorded at MH. As in the garden peat, at neither field Site was there a clear, consistent relationship between the water level and the depth of the upper limit of the sulphide zone. An analysis of variance on the MH data returned a highly significant result ($p<0.001$) for the effect of microhabitat on the water level and on the depth of the sulphide zone relative to the peat surface, and also for the individual buckets within each microhabitat. The same data showed no statistically significant seasonal effect. When the analyses were repeated on the MH sulphide zone data recorded relative to the water level, almost the reverse result was obtained; there was a significant ($p<0.05$) seasonal effect for each microhabitat, but no significant difference between individual buckets or between microhabitats. A linear regression of the depth of the upper limit of the sulphide zone on that of the water level, using all the MH data available ($n=111$), gave a coefficient of determination, r^2, of 0.67. At CR the individual bucket means were tested and gave results consistent with those for MH: a significant difference ($p<0.001$) between the three in terms of their mean water level and mean sulphide zone depth relative to the peat surface, but no significant difference between their mean sulphide zone depth relative to the water level. The (linear) correlation coefficient for the association between water level and sulphide zone depths at CR ($n=28$) was 0.87.

These analyses were carried out on limited data and it must also be remembered that although the silvered strips were placed as nearly as possible on each visit in their previous positions, the accuracy required for absolute comparability of successive records was not possible. In the light of these considerations it is worth examining the individual plots of Fig. 4.75 more closely, since analyses of

variance will tend to dampen extreme patterns in the data, an effect which will be more pronounced with a small data set.

There were differences in detail in the behaviour of the water level and sulphide zone depth between buckets, but in the pool cores at MH the sulphide zone generally remained about 5 cm or more below the water level, though occasionally it came up close to it. Of the 24 sulphide zone records made for MH pools, the sulphide zone was less than 5 cm below the water level on five occasions; in three August records and two for June (no field visits were made in July). Thus, the upper limit of the sulphide zone was much closer to the water level in the summer months than in spring or autumn. Unfortunately, there were no field records made for the winter period and so it is not possible to make a direct comparison with the interesting pattern of water level and sulphide zone behaviour noted in the M1 minibog. However, a similar pattern is suggested by the MH data. In 1982 the water level in the pools gradually increased in the autumn, but the sulphide zone either fell or remained steady. In 1983, in response (apparently) to more extreme water level fluctuations, the upper limit of the sulphide zone moved upwards along with the autumn water level changes, but the distance below the water level of the sulphide zone onset increased.

On four occasions, three in June 1983 and one in August 1982, the silvered strips recorded the upper limit of the sulphide zone to be at or above the peat floor of the pool. One record (June 1983) showed it to be about 8 cm into the water column. This apparently inconsistent behaviour of the sulphide zone relative to that of the water level was reflected by the very low correlation (0.26) for their association.

The MH lawn water levels apparently fluctuated over a smaller range than those of the pools, and the timing of the water level and sulphide zone fluctuations was slightly different from that of the pools. The 'hole' seen in the garden M1 winter data, and suggested by the MH pool data, appeared earlier in the year, in the autumn, under lawns. By May 1983 the sulphide zone had fallen below the water level again. The vertical distance between the two closed up between May and August (in one June record the sulphide zone was 4.5 cm above the water level) and then the gap widened again. Thus the 1983 lawn data

are more similar to those of the pools, but no records were made in October 1983, so it is not possible to be sure whether or not the 'hole' developed. The correlation coefficient for the lawn water level and sulphide zone association was 0.25.

As was the case for lawns, the water level in hummocks dropped sharply in 1982 between September and October records, and the drop was more extreme, as were all the fluctuations compared with lawns. Interestingly, and in marked contrast to the lawns, the sulphide zone changes did not parallel the drop, but continued to move upwards in the peat as they had done since June when the water levels began to rise. In all hummock buckets the sulphide zone thus began 5-10 cm *above* the water level in October. The three microhabitats at MH showed distinct patterns in their relative water level and sulphide zone positions at this time of year. The 1983 hummock data were less consistent. The 'hole' apparently began to develop from June onwards. The correlation for the linear association between water level and sulphide zone level was 0.48, and represents a two-fold increase in the correlation compared with that for the pools and lawns, respectively.

Of the three CR buckets used for sulphide zone records, two had water levels which fluctuated between ±7 cm around the peat surface, while the water level in the third lay between -12 cm and -25 cm. Thus all three ranged over 13-14 cm, but at different positions in the peat profile. In the two wetter areas the water level gradually increased over the two study years, with occasional deviations from this trend, indicating the usual seasonal pattern damped, presumably, by the resistance to drainage imposed by the buckets. In the drier peat core it is reasonable to assume that the fluctuations were less, if at all, affected by the bucket. In the drier cores the sulphide zone fluctuated with the water level, remaining between 3 cm (September) and 8 cm (May) below the water level in 1982. In 1983 the pattern was very similar. This pattern was similar to that seen in both years in the wetter buckets. In 1983 in the wetter areas there was evidence for the 'hole' developing from August onwards, and persisting until early summer; in June and August the sulphide zone was recorded between 0 cm and 2.5 cm below the water level in those

two cores. The pattern was less clear in the 1982 data, but there was still a tendency for the gap between the depth of the water level and sulphide zone to close up around June, and to increase from September.

It is also possible to interpret the results for 1982 in the wet cores somewhat differently. The water level and sulphide zone fluctuations in one bucket were apparently exactly out of phase, and a similar case could be made for the other wet core.

When multiple regressions were carried out to discover the relative importance of water level and temperature to sulphide zone movements (see below), there appeared to be a change in the importance of the water level, depending on the absolute temperature at the time of the records. This was investigated by dividing the data into those corresponding to temperatures below 5°C and those greater or equal to 5°C (the annual mean temperature at MH). Each of the seven temperature variables (Table 4.64) in turn was used as the determinant and, eliminating the data sets where n<7, this allowed 12 comparisons to be made between the correlation coefficients for the water level at times of the year when the temperature was below, or above, the annual mean. The full set of correlation coefficients for these analyses is given in Appendix Pa. The resulting data sets for the colder times of year (<5°C) are limited because of the timing of the field visits, and because there were limited data, it was not possible to split them further and look at the individual microhabitat effects. Of the 12 comparisons, seven indicated a drop of between 10 and 23% in the value of the water level and sulphide zone correlation coefficient at warmer (above average) times of year, one showed no change, and four showed an increase of between 1 and 22%. Correlation coefficients for the three comparable data sets (MH, CR and MH & CR) ranged from 0.79 to 0.89 when the temperature was above the mean, and from 0.74 to 0.95 when it was below. Hence it is not clear from these results how the significance of the association between sulphide zone and water level changes with temperature.

b) Short-term

In 1981, before the siphon overflow system had been installed in the garden peat, there was a period of continuous heavy rainfall lasting for 10 days. To determine whether the increase in water

levels had resulted in an elevated sulphide zone, a silvered strip was placed into the peat in H1 and H12 on 13 March as close as possible to the point where a strip had been placed on 12 February. The strips were removed 2 days later. The sulphide zone on the H1 strip began 11 cm below the peat surface compared with 20 cm previous to the inundation. The discolouration of the H12 strip began at -12 cm.

This result further supports the case for a relationship between the sulphide zone and water level, and gives a maximum microbial response time in this (isolated) case of 12 days. The microbial response to an increase in water level is probably considerably faster than this.

RELATIVE IMPORTANCE OF TEMPERATURE AND WATER LEVEL ON SULPHIDE ZONE DEPTH

Multiple regressions were carried out for P1, L1, H1 and M1 in turn, using data from all stages of the garden experiment together. Three analyses were tried for each microhabitat in turn, regressing the depth of the sulphide zone (w.r.t. peat surface) on the water level (w.r.t. peat surface) and, for the three successive analyses respectively; the median M2 air-peat interface temperature for the 2d sampling period, the mean of the daily M2 interface temperatures since the previous sulphide zone record, and the predicted mean temperature at -30 cm for the period since the last record (based on the garden sine wave equation in Appendix G, see Fig. G.9a).

Garden pool data (P1) did not give a significant result for any of the three regressions. Lawn sulphide zone behaviour was no better described by a multiple regression approach; in each case only the water level variable was significant, resulting in the degree of association already discussed above. A similar result was obtained for the hummock data, except that the value of r^2 was very slightly improved from 0.73 to 0.76 when the median interface temperature for the 2d sampling period was regressed in addition to the water level variable. The significance of the regression remained at the $p<0.001$ level, the individual variables being significant at the $p<0.0001$ and $p<0.046$ levels for water level and temperature, respectively.

Sulphide Zone

In the Minibog individual variable linear regressions returned low values of r^2, the individual temperature variables accounting for more of the variation in the S^{2-} zone fluctuations than that of the water level, but then returning a maximum r^2 value of only 0.28 (for the mean M2 interface temperature since the previous record). The multiple regression approach improved the r^2 values. The most significant multiple regressions of the three ($p<0.0001$) resulted when the mean temperature for the period since the previous record was involved. There was apparently no difference between the influence of either the mean interface temperature or that predicted at -30 cm in the peat; both were significant at the $p<0.0001$ level compared with $p<0.001$ for the water level variable, and both returned r^2 values of about 0.60 for the regression. The r^2 value was improved to 0.76 for the analysis involving the median interface temperature over the 2d sampling period ($p<0.001$).

Thus, in M1, where the water level was left to fluctuate naturally, the overriding influence on the depth of the sulphide zone was the mean temperature of the peat, with water level of secondary importance, though still highly significant. In the P1, L1 and H1 peat cores where the water level was regulated, the relationship between the variation in sulphide zone depth and the water level was by far the most important factor and this relationship was little better described by including a temperature factor.

Correlation coefficients for the association between water level and sulphide zone depth were ≥ 0.84 for the complete MH & CR data set (0.84 for CR and 0.82 for MH). When individual microhabitat data were investigated, and thus much of the variation in water level of the overall site data sets removed, the importance of the water level dropped dramatically ($0.22 \leq r \leq 0.48$) and temperature became relatively more important, although it accounted for only a small proportion of the variation in sulphide zone depth. Of the three microhabitats (full data sets), the association of sulphide zone with water level and temperature in the hummocks was different from that in the lawns and pools; the influence of the water level was more important than that for the overall site data.

RESULTS - CHEMICAL CHARACTERISTICS OF PEAT PROFILES

In the warmer periods of the year (represented by the restricted data sets) the absolute importance of the temperature and water level increased, apparently beyond that which might reasonably be attributable to the reduced size of the data set. The importance of the water level relative to that of the temperature increased in the hummocks whereas in pools and lawns water level was relatively less important than it was at cooler times, or in warmer times in the hummocks.

Appendix Pb gives the r^2 values for the regression equations for the depth of the sulphide zone on the water level variable combined with one or more temperature variables. The highest r^2 values for both the full Site and full microhabitat data sets were obtained with a combination of surface and shallow peat temperature variables in addition to water level. The variation in the Site sulphide zone data was more fully accounted for ($0.69 \leq r^2 \leq 0.82$) than that of the individual microhabitats ($0.00 \leq r^2 \leq 0.48$). When considering the Site data, the variation in sulphide zone depth was only slightly less well accounted for by a combination of water level and predicted peat temperatures compared with that of water level and surface temperatures. However, there was a much larger reduction in the r^2 value obtained for pools and lawns when predicted peat temperatures were substituted for surface temperatures; pool r^2 values dropped by about 50% (relatively), and lawns by about 80%. Hummocks were intermediate between Sites and the other two microhabitats in this respect also.

All results from the restricted data sets suggested a closer relationship between sulphide zone depth and a combination of water level and surface temperatures than between sulphide zone depth and predicted peat temperatures, the corresponding increase in r^2 values being between about 3 and 20%. Whether this is real, or whether a result of the inherent inaccuracies of the predictions is not possible to determine.

CHAPTER 5

QUANTITATIVE DISCUSSION

A man should never be ashamed to own he has been in the wrong, which is but to say in other words that he is wiser than was yesterday.

Jonathan Swift

QUANTITATIVE DISCUSSION

5.1 INTRODUCTION

The primary aim of this study was to obtain *in situ* measurements of methane and carbon dioxide concentrations over the full peat profile, and to use these, the main products of anaerobic microbial respiration, to estimate the rate of their production, and hence anaerobic decay, down the profile. This is the first time that such a study has been undertaken for deep peat. As already discussed in Chapter 1, previous workers interested in peat decay and accumulation have concentrated, in the main, on measuring aerobic decay and processes in the acrotelm (e.g. Dowding 1974; Rosswall, Veum & Kärenlampi 1975; Coulson & Butterfield 1978; Heal, Latter & Howson 1978). Fewer studies have been concerned with those same processes in the anoxic conditions of the catotelm and in most cases consideration of these has arisen following the results of studies similar to those above, in which decomposition was measured down to -30 cm or so, and which therefore indicated a depth-dependent decay rate (e.g. Heal *et al* 1974; Rosswall 1974). A short summary of the current understanding when the present study was undertaken of the effect of depth on decomposition in tundra is given by Heal *et al* (1981). The neglect of the catotelm has largely stemmed from the practical difficulties posed by working on a deep, anoxic system, and partly from the general belief that, at most, processes in the catotelm are so slow and slight in extent compared to those in the acrotelm, that they are negligible (e.g. Coulson & Butterfield 1978).

From the work of those interested in decay in peatland systems, there was evidence to show that the rate of decay fell (in some cases by up to two orders of magnitude or more) when material was engulfed by a rising water level and became incorporated into the catotelm (e.g. Clymo 1965; Gore & Olson 1967; Heal *et al* 1974; Williams 1980; Heal *et al* 1981). In their synthesis of MH decomposition studies, Heal, Latter & Howson (1978) reported that losses declined by 3-6% cm^{-1} over the top 20 cm of the profile. To some, this confirmed their ideas that processes in the catotelm were insignificant, but other workers (notably Gore & Olson 1967; Clymo 1978, 1983, 1984 and

Jones & Gore 1978) were prompted to consider further the rôle of the anoxic part of the system in the overall decay and accumulation process. Much of this work was theoretical. Models (including simulations) were produced in an attempt to describe the events mathematically (Bunnell & Dowding 1974; Bunnell & Tait 1974; Svensson & Rosswall 1980), but anaerobic decay was often neglected. For example, the ABISKO II model (Bunnell & Scoullar 1975) is restricted to processes in the top 10 cm of peat (or soil). The simulation incorporates 45 transfers and, in evaluating it in 1981, Bunnell & Scoullar wrote that "...a relatively complete carbon budget can be simulated." Yet no process occurring below 10 cm had then been incorporated. Earlier, in 1976, Flanagan & Bunnell presented the results of their efforts to model decomposition in tundra. However, they had assumed that "...the evolved CO_2 closely reflects the decomposition process and rate" and that carbon accumulation could be estimated from a knowledge of microbial biomass and annual productivity, respiration and annual primary productivity. This situation arose at least partly because the models were based on field studies and laboratory analyses, and hence were restricted by the assumptions inherent in the data. In 1985 Yarrington & Wynn-Williams, working on Signy Island, South Orkney, discovered significant discrepancies between their (aerobic ecosystem) model predictions for carbon cycling and the field-measured overall decomposition rate. They subsequently embarked on a closer investigation of the anoxic, methanogenic, part of the system.

Some *in situ* measurements of decay have previously been made, but only down to depths of about -25 to -30 cm. At these depths, in most systems, the water table will have been crossed, but it is likely that at least some of the measurements were made in the zone of peat which experiences fluctuating water levels, that is, in the transition zone between the acrotelm and catotelm. Furthermore, workers often used litter bag techniques, the short-comings of which in the present context have been touched on in Chapter 1.

More recently interest has grown in the rôle that methane plays in the carbon cycle, and has prompted an increase in studies of methane fluxes from various ecosystems. A considerable amount of

surface flux work, concerning both methane and carbon dioxide, has been carried out on a range of wetlands (Yamane & Sato 1961 (paddy fields); Flanagan & Veum 1974 (wet meadow, lichen heath, snowbed, *inter alia*); Harriss, Sebacher & Day 1982 (swamp)) and tundra, or other, peat systems (Clymo & Reddaway 1971; Svensson 1980; Svensson & Rosswall 1984; Luken & Billings 1985). The results from surface flux monitoring reflect the integrated, net flux from all processes within the substrate. They are a useful measure when considering net carbon cycling through the system, but on their own tell us little about the production, and the processes responsible, in different parts of the substrate. The chemistry (and the physics) of peatlands differs somewhat from freshwater sediments (Goodwin & Zeikus 1987), and, depending on the origin of their water, peatlands will differ in their chemistry (Damman & French 1987)). Nonetheless there are useful generalisations which can be learned from one and applied, with caution, to others.

In Chapter 1 the idea was introduced that the anaerobic decay rate in deep peat might be very low, but *not* insignificant. Clymo (1983, 1984) discussed this at some length and examined the theoretical model of accumulation presently under consideration (equation (5), Chapter 1). Regarding the question of the anaerobic decay rate in the catotelm, he used Scandinavian age-depth data in the model and derived anaerobic decay rates (Clymo 1984). They were indeed very small (6.5×10^{-5} y^{-1} < α_c < 5.5×10^{-4} y^{-1}). With such support for the theory of low anaerobic decay rates, he went on to a consideration of how mass was lost from the system.

The hydraulic conductivity of peat varies, and it is not yet possible to predict values from a knowledge of the physico-chemical nature of the peat concerned. However, there is general agreement that it is dependent, in part, on the botanical composition, bulk density and degree of humification of the peat (Rycroft, Williams & Ingram 1975a & b), and that there is a significant reduction in hydraulic conductivity on moving from the little-humified acrotelm down through the highly humified catotelm (though at least one report in the literature (Chason & Siegel 1986) conflicts with this generalisation). Conductivity may be reduced by several orders of

magnitude, reaching values as low as 10^{-8} cm s^{-1} in highly humified peat (Rycroft, Williams & Ingram 1975a). Clymo (1984) showed that, because of the highly humified nature of peat in the catotelm and the consequential small hydraulic conductivity there, removal of dissolved gas by mass flow is likely to account for only a negligible amount of the total carbon lost from the system each year. He then examined the possibility that diffusion could account for the loss. Making a number of assumptions, mainly that all the decayed matter was transformed into methane and carbon dioxide, and that this diffused upwards from its production site according to the analagous mathematics of heat flow (as described by Carslaw & Jaeger (1947) and modified by Clymo (1984)), Clymo showed that diffusion could transport the yearly carbon loss out of the system but that, if his estimate of its production rate was correct, methane would soon reach super-saturation concentrations in the peat and bubbles would probably form and supplement diffusion. He calculated the expected methane concentration profiles in different total depths of peat, resulting from a given, constant and continuous, production rate, after different time periods. The calculations suggested several interesting features of such profiles which can now be evaluated using the measured methane concentrations.

5.2 MODEL EVALUATION - GAS CONCENTRATION PROFILE SHAPE

The calculated methane concentration profiles showed an increase in concentration with depth. The greatest proportional rate of increase was over the top few centimetres of peat, down to about -50 cm, below which it slowed. The profile shape was similar as calculated after one year, one hundred years or an infinite time period, but over time the entire profile moved asymptotically towards a steady state. As already noted in Chapter 1, the absolute methane concentrations at any given depth, that is the position of the profile along the concentration axis and its precise shape, is dependent on the total peat depth: deeper peat deposits show higher overall concentration profiles, but as with time, the difference is reduced as the total depth increases. According to the calculations, the

concentration of methane could reach the limit of its solubility in water in one year at -50 cm and deeper, and after 10 years up to within -10 cm of the surface. Assuming continued decay and methane production, the calculations predict that within a very short period, relative to the known age of blanket bogs, the peat would become super-saturated with methane.

How do these theoretical predictions match up to the measured profiles of methane concentration at MH and CR (Fig. 4.53)?

The general shape of the measured methane concentration profiles is close to that predicted, with a steep increase between -20 and -50 cm, and then a slackening-off of the increase and a tendency towards a steady concentration deep in the peat. The deep peat concentration appears more variable at CR than at MH. This may be an artefact caused by the uneven distribution of samples from each depth, and in particular by the single sites each representing -3.0 m and -5.0 m.

The measured profiles also agree with those calculated in that the methane concentrations at CR (deeper average peat depth) were somewhat higher than those at MH.

The measured concentration profile shape thus corresponds well with expectation, and this gives some confidence in the model as a reasonable representation of a significant diffusion contribution to gaseous carbon loss from the peat.

The increase in methane concentration downwards in peat might be explained in one of two ways; either an increased rate of production there, or a decreased rate of diffusion (or a combination of the two). The calculations which produced the *theoretical* concentration profiles (Clymo 1984) were based on the assumption that both methane production rate and diffusion are constant, yet they too showed the shallow peat increase in concentration. Hence, a fall-off in concentration at the surface does not necessarily imply either an increase in diffusion or a fall-off in production. The similarity in the shapes of the theoretical calculations show that, even if diffusion is constant, and with a continuous, constant, methane production rate, the concentration of methane near the surface will be lower than that deeper down. Now suppose that these conditions hold just for the

surface peat; that is, even with continued production, diffusion is able to remove sufficient methane in the surface layers to produce the significant concentration decline, but deeper in the profile there is no further production of methane, though diffusion may continue. With time, the methane-depleted peat, initially forming the surface layer, would gradually come to form an ever-deeper portion of the profile, but there would be no means by which its methane concentration could *increase*. Indeed, if there were no further production, the resultant profile would probably show a reduction of the methane concentration deep down compared with that near the surface. After a very long time (strictly, $t \Rightarrow \infty$, but in practice the model predicts negligible (for our purposes) differences in results for $t > 1000$ y - well below the age of the deep peat under consideration here) the heat flow / diffusion model equation reduces to:

$$C = \frac{GZ(2Z_c - Z)}{2D} \qquad (11)$$

(Clymo 1984, modified from Carslaw & Jaeger 1947) where C is the methane concentration, G the methane production rate, Z_c the total depth of the catotelm and Z the particular depth being considered. From this equation it is clear that, if the methane production rate were zero, i.e. G=0, then after a thousand years there would be virtually no methane left. This is evidently not the case, and we are therefore left with no other conclusion than that methane production *does* continue at depth. It is *not* fossil methane, but modern (though formed from fossil solids). Until recently it had largely been assumed that methane emissions were probably the result of escaping fossil gas, but workers studying methane emissions from freshwater sediments (Johnston, Holding & McCluskie 1974) and peatlands (Williams & Crawford 1984) have now been led to the same conclusions of modern origin. Hence, decay does continue throughout the peat profile, and, having validated the general basis of the model in equation (11), we can proceed to use it for a closer examination of the measured methane profiles and their significance.

5.3 ACCURACY OF MEASURED GAS CONCENTRATIONS

First, consideration should be given to two matters which relate to the calculations which follow, and to the interpretation of the results. They concern the gases used to inflate the samplers, and the importance of any carbon losses which are due to bubble evolution. The concentration of both methane and carbon dioxide were apparently higher when N_2 was used to fill the sampler compared with when air was used. In the case of methane this could be due to a toxic effect of oxygen on the bacteria concerned, or to oxidation of the methane already present, and possibly, if oxygen were not having a toxic effect, also of that continually being produced. According to Kosaric & Jakic (1974), citing Söhngen (1906), aerobic methane-oxidising bacteria have been known at least since 1906. They have been reported more recently from a number of waterlogged substrates (Davis & Yarbrough 1966; Barnes & Goldberg 1976; Reeburgh 1980; Zehnder & Brock 1980; Iversen & Blackburn 1981; Van Cleemput & El-Sebaay 1985), including peat (for example, Bunnell, MacLean & Brown 1975; Williams 1980), and Svensson & Rosswall (1984) were led to the possibility of the existence of "microaerophilic methane oxidisers" to explain some of their results from Stordalen peat. Both aerobic (Kosaric & Jakic 1974; Van Cleemput & El-Sebaay 1985) and anaerobic (Davis & Yarbrough 1966; Reeburgh 1980; Zehnder & Brock 1980; Iversen & Blackburn 1981) biological methane oxidation have been reported. Several workers have concluded that methane production and oxidation can, and do, occur simultaneously; for example in anaerobic freshwater sediments (Zehnder & Brock 1980), and marine sediments (Barnes & Goldberg 1976; Iversen & Blackburn 1981). The quantities of methane involved are not insignificant; Zehnder & Brock (1980) estimated that about 2% of the methane produced (at pH 7) in an anoxic freshwater sediment was oxidised, anaerobically, over 99% of the product being CO_2. The proportions were constant, under varying experimental conditions. Methane oxidisers were also implicated (Granhall & Selander 1973) in high CO_2 production through stimulation of algal photosynthesis at Stordalen. Van Cleemput & El-Sebaay (1985) considered oxidation to be the most important transformation of CH_4. Williams (1980) cites

Jannasch (1975) and Indrebo, Penegerud & Dundas (1979) to point out that in some lakes the rates of methane production and oxidation cancel one another out. The possibility exists, therefore, that the oxygen in the sampler air allowed an increase in the rate of methane oxidation.

There is then the consideration of oxygen toxicity to the obligately anaerobic methanogens in the peat. Zehnder & Wuhrmann (1977) found that methanogens were not killed by high (≃ 20% v/v or ≃ 300 ppm) oxygen concentrations, but that 0.0007% (or 0.01 ppm) of dissolved O_2 completely inhibited growth and methane production. Zehnder & Brock (1980) aerated an anoxic freshwater sediment and found that methane production and oxidation were inhibited, and began only after oxygen tension was reduced. Dworkin & Foster (1956), working on a methanogen which inhabits the intracellular parts of *Elodea canadensis*, found that oxygen was toxic at about 20% (v/v) concentration. Bunnell, MacLean & Brown (1975) attributed the fact that little CH_4 was evolved from the soil surface of the tundra at Barrow, Alaska, to the activity of CH_4-oxidising bacteria, but noted that the situation was different if soils were perturbed.

It would seem, therefore, that the most likely cause of the discrepancy between air- and N_2-filled sampler results is an inhibitory effect of oxygen on methanogenesis. However, it is unlikely that a single mechanism is responsible; it is far more likely that, given the complex nature of the peat substrate and the diverse microflora therein (Collins, D'Sylva & Latter 1978; Williams 1980) that many interrelated microbial activities are contributing.

As noted earlier, not only the concentration of CH_4 collected from N_2-filled samplers but also that of CO_2 was higher than that from air-filled ones. Of the two types of methanogens (Appendix M), those which metabolise acetate and produce CH_4 simultaneously produce CO_2. Thus it may not be altogether surprising that CH_4 and CO_2 concentrations appear to respond in parallel. However, it is unlikely that the full explanation is so simple. Appendix M shows that CO_2 is a product of metabolic reactions at almost every stage in the degradation of dead biomass, and the depressed CO_2 concentrations measured in air-filled samplers are likely to be an integral response

to numerous chemical events brought about by local aeration. To unravel the details is not possible here, and would involve much painstaking controlled experimental work. A fuller understanding of the reasons for the concentration differences measured would improve the interpretation of the data as a whole, but such refined information would seem yet to be some way off; peat chemistry (including microbial physiology) is even less well understood, and certainly less intensively studied, than are these aspects of freshwater and marine systems.

Secondly, bubble evolution. The solubility of methane (CH_4) in water is given in various published tables as somewhere between 10 and 32 ppm, dependent on methodology and conditions. Clymo (1984) assumed a value equivalent to 32 ppm (0.066 cm^3 cm^{-3} at 5 m) and for consistency and comparability the same value will be used here. The solubility limit of CH_4-C at atmospheric pressure corresponding to this is 12.5 ppm, and is plotted in Fig. 4.53.

It is clear from Clymo's (1984) Fig. 15 and Fig. 4.53 here, that the exact choice of which solubility value to use is not critical for our purposes. The important thing to notice is that the measured concentration of methane is many times (on average up to 8x) the theoretical solubility limit; the peat is super-saturated with methane. Under these conditions we would expect that bubbles would be formed. There are many accounts in the literature of gases bubbling up from the depths of stagnant ponds, marshes and other wetlands, including peat bogs (Rossolimo 1935, cited by Ehhalt 1974; King, Berman & Wiebe 1981; Sansome & Martens 1981). On most field visits during the present study gas bubbles were seen surfacing in pools and lawns as these were approached for sampling, especially in the summer months. Indeed it was with this phenomenon in mind that the current methodology for gas collection at the surface was adopted, to reduce the chance of erratic measurements which would result from bubble evolution caused by approaching the site immediately before sampling.

Although there are many references to bubble evolution from various wetlands, little quantitative work has been carried out to assess the importance of the phenomenon in terms of carbon loss. Workers have collected the bubbles and analysed them for the gases

they contain (CH_4, CO_2, O_2 and N_2; e.g. King, Berman & Wiebe 1981), and often comment on the assumed significance of the losses. For example, Hammond, Simpson & Mathieu (1975) conclude that diffusion of methane in sediments may be too slow to account for the observed flux and that bubbles may be a "major mechanism" for CH_4 transport out of sediments. Cappenberg, Hordijk & Hagenaars (1984) estimated from their measurements of methane flux by molecular diffusion and by bubble ebullition that bubbles accounted for between 1x and about 3x the mass of CH_4-C lost by diffusion from the sediments of Lake Vechten. Sansome & Martens (1981) noted that CH_4 losses by diffusion and by mass flow in bubbles from an anoxic coastal sediment were seasonal, and that bubbles were responsible for losses amounting to about 6x those attributable to diffusion.

It is possible, by comparing the measured methane concentration profiles from the present study (Fig. 4.53) with the theoretical concentrations reached at t_∞, and allowing for dissolution, to make a rough estimate of the relative losses attributable to diffusion and bubble evolution. The assumption that the peat profile has reached a steady-state depth is inherent in the calculations. To arrive at the theoretical concentration profile we use equation (11), above. However, we cannot simply substitute our G value into the equation to produce the concentrations because the G value is calculated by substituting in the measured concentrations. Clymo (1984, Fig. 15) calculated a theoretical concentration profile for t_∞, and we can adjust this as a first approximation. He used a G value for methane of 0.028 $cm^3\ cm^{-3}\ y^{-1}$ (n.t.p.) (0.94 $\mu g\ cm^{-3}\ y^{-1}$) and a value of D of 500 $cm^2\ y^{-1}$. According to equation (11), C is directly proportional to G and inversely proportional to D. Thus, if we adjust Clymo's theoretical steady-state methane profile concentrations by a factor of 0.98 ((0.50/0.94) x (500/270); see below for origin of figures) we arrive at an independent estimate of the steady-state concentration profile. In practice, interestingly, since the two calculations are based on different parameter values, themselves arrived at by independent methods, there is no difference, and either set of figures gives a theoretical deep peat (Z > 250 cm) concentration of 180 $\mu mol\ cm^{-3}$ CH_4-C, or 2160 $\mu g\ cm^{-3}$ CH_4-C. This compares with the *measured*

concentration in peat at this depth (Fig. 4.53) of 100-120 μg cm^{-3} CH_4-C (≈ 5%).

It is important to remember that these are rough estimates, but it would seem that to assume the measured concentrations reflect methane production rates at the corresponding depth is probably to underestimate the real situation. Losses by diffusion probably account for the general shape of the methane profile, but the additional mass lost through bubble evolution may be considerable.

5.4 GAS PRODUCTION RATES

Keeping in mind that the results will be minimal estimates (based on losses due to diffusion alone), we can substitute the measured gas concentrations into equation (11) to calculate the methane production rates at the depths from which gas samples were collected. Exactly the same calculations were followed to produce CO_2-C production rates. The resultant G values for CO_2-C are not underestimating the true production rate to the same extent as those of CH_4-C, since all the CO_2 produced would be able to dissolve (Fig. 4.55). In the calculations Z_c, strictly the total depth of the *catotelm*, was taken as the total peat depth at the site concerned, as shown in column A of Table 3.4. The value of Z used was the nominal sampler depth. The diffusion coefficients used were 270 cm^{-2} y^{-1} and 333 cm^{-2} y^{-1} for CH_4 and CO_2, respectively (Table 4.2).

The mean CH_4-C and CO_2-C production rates were calculated for those data groups which, according to the results in Tables 4.41, 4.42 and 4.43 were insignificantly different and for which grouping together was therefore statistically valid. The results are given in Tables 5.1 and 5.2. If the value of 500 cm^2 y^{-1} for the coefficient of diffusion of methane had been used in the calculations here, as for Clymo's (1984) calculations, the reported methane production rates would be increased by a factor of 500/270, or roughly doubled.

The Tables indicate a considerable range of gas production rates (and therefore decay) over the peat profile.

Whilst at MH the methane production rate tended to increase with increasing peat depth, though somewhat erratically and inconsistently,

at CR the rate decreased with depth. Such differences are not evident from a comparison of the *concentration* profiles (Fig. 4.53). Williams & Crawford (1984) found that CH_4 production rate decreased with depth, but with an increase at the base, in an acid Minnesota peatland. At both sites used for the present study, there was evidence of a peak in production at between -20 cm and -50 cm, and, particularly at Moor House, the peak occurred at -50 cm (or rather the maximum production rate was calculated from the -50 cm sample which indicates a peak probably somewhere between -20 cm and -50 cm).

Turning to CO_2-C production rates, at both MH and CR, in general, there was a reduction with depth. Maximum production was calculated from the -20 cm samples; that is, at a slightly shallower depth than the -50 cm peak in CH_4-C production.

Thus the methane and carbon dioxide production profiles are in agreement with observations in the literature regarding the existence of a vertically-delimited zone (horizon) of peak microbial activity in anoxic freshwater sediments (e.g. Cappenberg 1974a; Zehnder & Brock 1980) and peat (e.g. Svensson & Rosswall 1984; Williams & Crawford 1984; Walton 1985). Although it is true to talk of sub-surface peaks in gas *production* and in microbial activity as if they were synonymous, more detailed studies of profiles of anaerobic microbial numbers and activity, and the *concentration* of their substrates and products in sediments and peat have indicated that the real situation is rather more complex, and that gas concentration and microbial activity are not equivalent measures. The position and significance of observed peaks will be considered in more detail in the following chapter.

5.5 DECAY IN THE CATOTELM

After calculating the individual (spot) gas production rates, a minimisation technique was applied to them (A Simplex routine called MINUIT, written by R. S. Clymo), to give a 'best-fit' mean value of G for the data set concerned. There was considerable variation in the measured gas concentrations, particularly those collected at -20 cm, and because these had the potential to distort the final result, they

TABLE 5.1 Methane production rates in peat at MH and CR. For details of calculations, see text. Mean values of G ($\mu g\ cm^{-3}\ y^{-1}\ CH_4$-C). Standard errors were between 3 and 92% of the means, with most below 25%. - indicates no reliable data; + indicates G < 0.05.

a) Moor House

Depth (cm)	site 1 mean	n	site 2 mean	n	site 3 mean	n
	Air-filled					
20	-		0.1	5	0.3	5
50	+	5	0.3	5	0.3	5
100	0.5	5	0.2	5	0.2	5
200-300	0.7	10	0.4	10	0.4	10
	N_2-filled					
20	-		0.3	7	0.6	7
50	+	7	0.9	7	1.0	7
100	0.5	7	0.5	7	0.5	7
200-300	0.7	14	0.8	14	0.8	14

At 20 cm only; N_2-filled; n=1 throughout

Date	25SP82	26OT82	14DC82	08AP83	16MY83	24JN83	05AG83	22SP83
site 1	-	-	-	-	-	-	-	-
site 2	+	0.7	-	0.6	0.4	+	+	+
site 3	+	1.0	-	1.4	1.5	0.2	+	+

b) Coom Rigg

Date	01DC81	n	02AP82	n	06MY82	n	23JN82	n	20AG82	n	25SP82	n	26OT82	n
Depth (cm)	Air-filled										N_2-filled			

TABLE 5.2 Carbon dioxide production rates in peat at MH and CR. For details of calculations, see text. Mean values of G (μg cm^{-3} y^{-1} CO_2-C). Standard errors were between 6 and 76% of the means, with most between 25 and 30%. - indicates no reliable data.

a) Moor House

Depth (cm)	site 1 mean	n	site 2 mean	n	site 3 mean	n
	Air-filled					
20	-		2.6	3	1.7	4
50	0.4	3	1.9	3	1.0	5
100	1.5	5	1.0	4	0.6	5
200-300	1.1	10	0.8	10	0.7	8
	N_2-filled					
20	-		2.6	7	1.8	7
50	0.3	5	2.3	7	2.0	7
100	1.2	7	1.2	7	1.2	7
200-300	1.1	14	0.8	13	0.8	14

At 20 cm only; N_2-filled; n=1 throughout

Date	25SP82	26OT82	14DC82	08AP83	16MY83	24JN83	05AG83	22SP83
site 1	-	-	-	-	-	-	-	-
site 2	3.1	3.8	-	2.7	3.2	1.4	0.7	3.2
site 3	2.5	2.6	-	2.2	3.0	0.7	0.4	1.5

b) Coom Rigg

Date	01DC81	n	02AP82	n	06MY82	n	23JN82	n	20AG82	n	25SP82	n	26OT82	n	Date
Depth (cm)	Air-filled										N_2-filled				Depth (cm)
20	1.2	5	2.4	4	2.9	5	2.5	4	4.1	3	4.9	3	4.0	3	20
50	1.1	5	1.4	5	2.9	5	2.7	5	2.6	5	2.7	5	2.8	4	50
100	1.1	5	1.0	5	2.2	5	1.7	5	1.8	5	1.8	5	1.5	5	100
200	0.9	4	0.5	5	2.0	5	1.3	5	1.3	4	0.8	11	1.5	10	200-500
250	0.1	1	0.3	1	0.4	1	0.6	1	0.6	1					
300	-	-	0.3	1	0.9	1	1.0	1	1.0	1					
400	0.2	3	0.2	3	0.5	3	0.5	3	0.4	3					
500	0.1	1	0.2	1	0.6	1	0.5	1	0.4	1					

Date	14DC82	n	08AP83	n	16MY83	n	24JN83	n	05AG83	n	22SP83	n
Depth (cm)												
20	3.2	4	3.1	4	3.4	4	4.0	4	4.2	4	2.0	3
50	2.3	5	2.2	5	2.1	5	2.7	4	2.6	5	2.0	5
100	1.6	5	1.6	5	1.5	5	1.6	5	1.7	5	1.7	5
200-500	0.7	11	0.6	11	0.7	11	0.6	10	0.7	10	0.8	10

All dates; N_2-filled

Depth (cm)	Mean	n
50	2.5	38
100	1.6	40
200-500	3.0	83

were omitted from the calculations. Much of the variation in the deeper concentration data was eliminated by first applying a smoothing technique: the median concentration from all field visits was obtained for every sampler at -50 cm and deeper at each site. Only data obtained from N_2-filled samplers were included in the analysis. Thus, the resulting G value for CH_4-C and for CO_2-C is the 'best-fit' mean production rate over the peat profile from -50 cm depth to the mineral base, and calculated from data collected using N_2-filled samplers and the respective coefficients of diffusion given above.

The analysis yielded values for G of 0.50 and 0.90 $\mu g\ cm^{-3}\ y^{-1}$ for CH_4-C and CO_2-C production, respectively. These represent the rates of gas production which, if they continue at a constant rate for a very long time (at least a thousand years, say, (see above)), and the gas moves away from the site of production by (upward) diffusion only, will result in a steady-state concentration profile of the form measured in the present study (Figs. 4.53 and 4.54) and predicted previously by theoretical considerations (Clymo 1984, including Fig.15). In order to maintain a steady-state concentration profile, gas production must equal its loss. If it is assumed that after about 7000 years (roughly the age of the peat systems under consideration here, Smith (undated)) a steady-state profile has been reached, and this is indeed to be inferred from Clymo's calculations, then we can equate the value of G obtained with the rate of loss due to diffusion from the peat body at -50 cm and below. It is then possible to estimate the total mean efflux of carbon as CH_4-C and CO_2-C per year from that portion of the profile, and to compare it with the annual loss from the entire profile, as indicated by the surface flux data. Thus we can estimate the contribution made by the anoxic peat to carbon losses as a whole.

In Table 5.3 are compared some results of calculations based on the values of G for CH_4-C (0.50 $\mu g\ cm^{-3}\ y^{-1}$) and CO_2-C (0.90 $\mu g\ cm^{-3}\ y^{-1}$) arrived at above. The results illustrate the contribution to total carbon lost from the system that is attributable to peat below -50 cm, the 'catotelm', and what proportion of this is lost through diffusion of CH_4-C and CO_2-C, respectively. They are

TABLE 5.3 A comparison of gas production rates between sites with contrasting environmental parameters. For further details, see text.

Table 5.3a

	Total Peat Depth	A		B	C		D			A + C	B + D	E					
		P_{CH_4}	R_{CH_4}		P_{CO_2}	R_{CO_2}		Origin	See Table	P_C	P_{CA}	P_{PC}	P_{PCH_4}	P_{PCO_2}	T_{PCH_4}	T_{PCO_2}	Comments
	(cm)	($\mu g\ cm^{-2}\ y^{-1}$)	($mg\ m^{-2}\ d^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	($mg\ m^{-2}\ d^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)			($\mu g\ cm^{-2}\ y^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	(%)	(%)	(%)	(%)	(%)	
a)	mean 320	159	16,8	613	285	176	6424	MH U	4,9	444	7037	6,3	35,8	64,2	2,3	4,1	Contrasting Sites. Site
	300	149	9,7	354	267	445	16243	CR site 16 U	4,13	416	16597	2,5	35,8	64,2	0,9	1,6	16 more minerotrophic?
b)	mean 320	159	16,8	613	285	176	6424	MH U	4,9	444	7037	6,3	35,8	64,2	2,3	4,1	Contrasting Sites (means)
	mean 360	179	17,0	621	320	278	10147	CR U	4,13	499	10768	4,6	35,9	64,1	1,7	3,0	
c)	340	169	16,9	617	303	213	7775	MH 4-6 U	4,31	472	8392	5,6	35,8	64,2	2,0	3,6	Contrasting sites
	300	149	7,8	285	267	190	6935	MH 7-9 U	4,31	416	7220	5,8	35,8	64,2	2,1	3,7	
	320	159	25,5	931	285	127	4636	MH 10-12 U	4,31	444	5567	8,0	35,9	64,1	2,9	5,1	
d)	mean 320	159	17,1	624	285	59	2154	MH pool U	4,29	444	2778	16,0	35,9	64,1	5,7	10,3	Contrasting surface
	mean 320	159	25,1	916	285	80	2920	MH lawn U	4,29	444	3836	11,6	35,9	64,1	4,1	7,4	microhabitats (acrotelms)
	mean 320	159	8,2	299	285	390	14235	MH humm U	4,29	444	14534	3,1	35,9	64,1	1,1	2,0	
e)	400	199	21,9	799	356	137	5001	CR site 13 U	4,13	555	5800	9,6	35,9	64,1	3,4	6,1	Contrasting total peat
	500	249	20,0	730	445	191	6972	CR site 14 U	4,13	694	7702	9,0	35,9	64,1	3,2	5,8	depths (and position on
	420	209	20,7	756	374	281	10257	CR site 15 U	4,13	583	11013	5,3	35,8	64,2	1,9	3,4	the bog)
	300	149	9,7	354	267	445	16243	CR site 16 U	4,13	416	16597	2,5	35,8	64,2	0,9	1,6	
	200	100	12,4	453	178	525	19163	CR site 17 U	4,13	278	20069	1,4	35,9	64,1	0,5	0,9	

Table 5.3b

	Total Peat Depth	A		B	C		D			A + C	B + D	E					
		P_{CH_4}	R_{CH_4}		P_{CO_2}	R_{CO_2}		Origin	See Table	P_C	P_{CA}	P_{PC}	P_{PCH_4}	P_{PCO_2}	T_{PCH_4}	T_{PCO_2}	Comments
	(cm)	($\mu g\ cm^{-2}\ y^{-1}$)	($mg\ m^{-2}\ d^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	($mg\ m^{-2}\ d^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)			($\mu g\ cm^{-2}\ y^{-1}$)	($\mu g\ cm^{-2}\ y^{-1}$)	(%)	(%)	(%)	(%)	(%)	
a)	mean 320	295	16,8	613	285	176	6424	MH U	4,9	580	7037	8,2	50,8	49,2	4,2	4,1	Contrasting Sites. Site
	300	277	9,7	354	267	445	16243	CR site 16 U	4,13	544	16597	3,3	50,8	49,2	1,7	1,6	16 more minerotrophic?
b)	mean 320	295	16,8	613	285	176	6424	MH U	4,9	580	7037	8,2	50,8	49,2	4,2	4,1	Contrasting Sites (means)
	mean 360	332	17,0	621	320	278	10147	CR U	4,13	652	10768	6,1	50,8	49,2	3,1	3,0	
c)	340	313	16,9	617	303	213	7775	MH 4-6 U	4,31	616	8392	7,3	50,8	49,2	3,7	3,6	Contrasting sites
	300	277	7,8	285	267	190	6935	MH 7-9 U	4,31	544	7220	7,5	50,8	49,2	3,8	3,7	
	320	295	25,5	931	285	127	4636	MH 10-12 U	4,31	580	5567	10,4	50,8	49,2	5,3	5,1	
d)	mean 320	295	17,1	624	285	59	2154	MH pool U	4,29	580	2778	20,9	50,8	49,2	10,6	10,3	Contrasting surface
	mean 320	295	25,1	916	285	80	2920	MH lawn U	4,29	580	3836	15,1	50,8	49,2	7,7	7,4	microhabitats (acrotelms)
	mean 320	295	8,2	299	285	390	14235	MH humm U	4,29	580	14534	4,0	50,8	49,2	2,1	2,0	
e)	400	369	21,9	799	356	137	5001	CR site 13 U	4,13	725	5800	12,5	50,8	49,2	6,4	6,1	Contrasting total peat
	500	461	20,0	730	445	191	6972	CR site 14 U	4,13	906	7702	11,8	50,8	49,2	6,0	5,8	depths (and position on
	420	387	20,7	756	374	281	10257	CR site 15 U	4,13	761	11013	6,9	50,8	49,2	3,5	3,4	the bog)
	300	277	9,7	354	267	445	16243	CR site 16 U	4,13	544	16597	3,3	50,8	49,2	1,7	1,6	
	200	184	12,4	453	178	525	19163	CR site 17 U	4,13	362	20069	1,8	50,8	49,2	0,9	0,9	

TABLE 5.3 (cont'd)

Notes

P_{CH4} Total annual production of CH_4-C in the 'catotelm' (below 50 cm depth), calculated as G_{CH4} x depth. (Column A).

R_{CH4} Surface flux of CH_4-C; represents the total CH_4-C loss from the acrotelm and catotelm. (Column B).

P_{CO2} As for P_{CH4}. (Column C).

R_{CO2} As for R_{CH4}. (Column D).

P_C Total carbon loss from the 'catotelm', calculated as the sum of CH_4-C and CO_2-C. Assume steady-state conditions, i.e. that loss = production.

P_{CA} Total carbon loss from the acrotelm and catotelm.

P_{PC} % total carbon loss attributable to the 'catotelm', calculated as 100(A + C)/(B + D). (Column E).

P_{PCH4} % P_C attributable to CH_4-C, calculated as 100A/(A + C).

P_{PCO2} % P_C attributable to CO_2-C, calculated as 100C/(A + C).

T_{PCH4} % total carbon loss attributable to CH_4-C from the 'catotelm', calculated as 100A/(B + D).

T_{PCO2} % total carbon loss attributable to CO_2-C from the 'catotelm', calculated as 100C/(B + D).

G_{CH4} = 0.50 $\mu g\ cm^{-3}\ y^{-1}$ CH_4-C for Table 5.3a and 0.922 $\mu g\ cm^{-3}\ y^{-1}$ for Table 5.3b.

G_{CO2} = 0.90 $\mu g\ cm^{-3}\ y^{-1}$ CO_2-C for both parts of the Table.

D_{CH4} = 270 $cm^2\ y^{-1}$ for Table 5.3a and 500 $cm^2\ y^{-1}$ for Table 5.3b.

D_{CO2} = 333 $cm^2\ y^{-1}$ for both parts of the Table.

mean values and do not indicate the extent of any variation. The Table shows five comparisons (a-e).

a) Effect of total peat depth on carbon loss

'Catotelmic' total carbon losses (column A + C in the Table) appear to be directly proportional to total peat depth, but this result is, in part, a consequence of the simplifying assumptions of the mathematics: gas production (= loss) for each total peat depth was calculated as the product of depth and a constant production rate, G, for each component, and then the two figures were summed to give total carbon loss. However, although the direct proportionality is an artefact, the positive association between total peat depth and absolute total carbon loss from the 'catotelm' is real, and is a consequence of continuing decay throughout the peat profile, as described earlier. Thus total carbon losses from the 'catotelm' increase with total peat depth (cf the *decrease* in gas *production* rates shown in Table 5.1).

Results reported in the previous chapter (Surface Gas Flux - The Effect of Total Peat Depth, and Fig. 4.21) indicated that, in general, methane efflux from intact sampling areas at CR increased, and that of carbon dioxide decreased, with increasing total peat depth. The total amounts of CH_4-C involved are so much smaller than those of CO_2-C (compare columns B and D in Table 5.3) that when the two are combined, the CO_2-C trend relative to the total depth prevails for the total carbon losses from the catotelm and acrotelm together; there is a tendency towards an inverse relationship between total depth and total carbon loss. The combined effect of an increasing absolute annual carbon loss from the catotelm with increasing total peat depth, and a concomitant decreasing total carbon loss, leads to a direct relationship between total peat (or catotelm, assuming the acrotelm depth is constant) depth and the *proportion* of the total system carbon lost each year from the catotelm (Column E of Table 5.3). This is in agreement with expectation, given that decay continues throughout the profile. The relationship is not perfect. This is due in part to the imperfect associations between total peat depth and CH_4-C, and total depth and CO_2-C, the effects of which are combined when proportional contributions are considered. In the consideration of surface flux

trends in the previous chapter, it was reasoned, from a comparison of cut and intact area results, that at least some of the effects seen at the surface were attributable to processes within the catotelm, and the present calculations support this conclusion. Further, total peat depth is not the only variable involved. In practice the required variation in total depth was achieved through sampling different peat profiles, and thus each profile will also differ in its chemical and physical properties. As was noted in the case of surface flux, the trends in the results could be interpreted in terms of position of the sampling area on the bog (Chapter 4, Surface Gas Flux - Effect of Total Peat Depth, and Fig. 4.21, and such is the case here, too. Whereas total annual carbon losses from the catotelm alone are, apparently, directly associated with total peat depth (column A + C in Table 5.3), annual total carbon losses from the catotelm and acrotelm combined are directly associated with the position of the sampling area on the bog (column B + D in Table 5.3). It is possible to speculate at length about the cause or, more likely, the combination of causes, which lead to this being so. For example, it has been found (e.g. Svensson, Veum & Kjelvik 1975; Svensson & Rosswall 1984; Williams & Crawford 1984) that decay is relatively high where conditions are more minerotrophic, and this interpretation could go part way to explaining the trends seen here for the relationship between site position and carbon losses.

In accordance with the relative production rates, G, of CH_4-C and CO_2-C, the proportion of catotelm carbon losses attributable to CH_4-C and CO_2-C is 36% and 63%, respectively, although, as can be seen from the last two columns of figures in Table 5.3, there is variation in the absolute amounts lost. If it is assumed that total decay of material results in a 1:1 ratio of CH_4-C : CO_2-C, and that at depths of -50 cm and more there is no methane oxidation (which is not necessarily so), such that the original proportions remain, the inference is to be made that bubbles account for 43% of the total methane losses. Note that this is at variance with the earlier calculation which suggested that bubble evolution might be responsible for 10x the CH_4-C losses from the catotelm compared with diffusion.

Nothwithstanding the lack of accurate figures, we are once again led to conclude that bubble evolution is probably highly significant.

Sites with similar total peat depths may show very different absolute annual carbon losses (column B + D, case a)). Closer examination reveals that the large discrepancy is a result of differences in carbon losses from the acrotelm rather than from the catotelm (cf columns A + C and B + D, case a), and in consequence the proportional carbon loss from the catotelm (expressed relative to the total carbon loss) will vary beyond what might be expected from a comparison of the total peat depths alone (column E, case a)). Such large differences suggest significant variation in peat or surface vegetation characteristics, and this is supported by a comparison between mean Site values (rather than between the individual sampling sites at each Site which have similar total peat depths (case a)) shown in the Table (case b). In this way extremes are removed, and smaller differences arise between the proportional contribution of the catotelm to total annual carbon losses from different Sites, despite larger differences in the mean total peat depth (column E, case b).

b) Proportional contribution of the catotelm to total carbon loss

The variation in total system carbon losses, and the proportional contribution of the catotelm at different sampling areas within a single field Site (MH) are illustrated in comparison c). Proportional carbon loss attributable to the catotelm ranged between 5.6% and 8%. Much larger differences arise if comparisons are made between the three microhabitat types at MH (case d).

Table 5.3a shows clearly the complex nature of gas production in peat, even when the real situation is simplified to the point that a single production rate for each of methane and carbon dioxide is assumed to operate throughout the whole anoxic peat body, there is considerable variation in the proportional contribution of methane and carbon dioxide to total carbon losses from the peat profile. The Table shows that there is no simple relationship between total peat depth and the proportional contribution made to total carbon loss by the 'catotelm', even though the results arise from calculations based on a single mean gas production rate throughout the 'catotelm' (G) for each component, itself a product (in the mathematical sense) of the

diffusion rate, D. Thus the use of a different diffusion rate will produce a fractional change in the value of G for each gas, and in the corresponding figures to those calculated in Table 5.3a. The relative contribution of CH_4-C and CO_2-C to total carbon loss from the 'catotelm' is a direct reflection of the ratio between the calculated gas production rates of CH_4-C and CO_2-C, which would thus be affected by use of different values of D. Further, since diffusion rates are not involved in calculating surface flux, using different D values would produce different results for the proportional contribution of the 'catotelm' carbon to the total system carbon loss. Table 5.3b has been drawn up using the value of D for methane used by Clymo (1984) (500 $cm^2\ y^{-1}$, cf 270 $cm^2\ y^{-1}$ in Table 5.3a). This gives a production rate of 0.922 $\mu g\ cm^{-3}\ y^{-1}$ CH_4-C. The value of D for CO_2 has not been altered from that used in drawing up Table 5.3a, and hence CO_2-C production rate remains as 0.90 $\mu g\ cm^{-3}\ y^{-1}$. The most important effect is to increase the proportional contribution of CH_4-C to the 'catotelm' carbon loss, and hence also that of the total catotelm carbon loss relative to that from the whole system. In certain, controlled, situations the CH_4-C : CO_2-C ratio may be used as a clue to the nature of the substrates involved in the metabolic breakdown of the peat. Thus, for other (microbiological and thermodynamic) studies, an accurate knowledge of the diffusion rate of CH_4-C and CO_2-C could be important.

c) Calculation and evaluation of the anaerobic decay rate, α_c

Using the calculated values of G, and again assuming that total carbon loss is equal to the sum of losses attributable to CH_4-C and CO_2-C, we can estimate the anaerobic decay rate, α_c, according to $\alpha_c = G_c/\rho_c$, where G_c is equivalent to the sum of G_{CH4} and G_{CO2}, and ρ is the mean bulk density of the peat concerned in terms of carbon rather than the usual 'CH_2O'. Using the initial values of G given above for CH_4-C and CO_2-C, the carbon loss from the 'catotelm', G_c, is 1.40 $\mu g\ cm^{-3}\ y^{-1}$. Comparing this with a bulk density of $3.59 \times 10^4\ \mu g\ cm^{-3}$ C ($\equiv$ 0.088 g cm^{-3} CH_2O) (Fig. 2.4) gives $\alpha_c = 3.9 \times 10^{-6}\ y^{-1}$.

This is the first time that the anaerobic decay rate in peat has been calculated on complete profiles of *in situ* peat gas

concentrations. The exact result is, of course, dependent on the choice of values to use in the calculation. Specifically, α_c varies with changes in bulk density and gas production rate. The value of 3.9×10^{-5} y^{-1} is based on the mean bulk density value (0.088 g cm^{-3} CH_2O, as carbon) calculated for all MH and CR cores between -50 cm and the base of the peat (n=309). Values of ρ, again as carbon, ranged between 0.015 g cm^{-3} and 0.074 g cm^{-3}, which give α_c, respectively, as 9.3×10^{-5} y^{-1} and 1.9×10^{-5} y^{-1}.

Alternatively we could vary the value of G in calculating α_c. G is itself dependent on D, C, Z_c and Z, of which the greatest uncertainty lies in the exact value of D. If the experimentally determined values of D for CH_4-C and CO_2-C from the present study are used (270 cm^2 y^{-1} and 333 cm^2 y^{-1}, respectively), as for Table 5.3a, along with the mean bulk density value, the total carbon loss from the catotelm is as calculated above, 1.4 µg cm^{-3} y^{-1}. If the value of D_{CH4} is taken as 500 cm^2 y^{-1} (as in the calculations of Clymo 1984), and all other values remain unchanged, the resultant carbon loss is calculated to be 1.82 µg cm^{-3} y^{-1}. Comparing these losses with the mean bulk density gives α_c in the first case as 3.9×10^{-5} y^{-1} (the same calculation as previously), and in the second as 5.1×10^{-5} y^{-1}. A change of 35% in the value of D results in 24% change in the value of α_c; in absolute terms the effect on α_c is small. The resultant values fall within the range calculated by Clymo on different occasions: model estimates (28 parameter sets) yielded values between 0.4×10^{-7} y^{-1} and 0.5×10^{-2} y^{-1} based on data from age and bulk density profiles for MH blanket peat, with most values falling between 10^{-5} and 10^{-2} y^{-1} (Clymo 1978). Applying the same model to Abisko (N. Sweden) data gave α_c equal to 10^{-5} y^{-1}. In the same paper, α_c was calculated from measured methane and carbon dioxide evolution from the surface of Burnt Hill; the resultant value was 10^{-5} y^{-1}. Applying different versions of essentially the same model to Scandinavian age-bulk density profiles gave estimates of 2×10^{-4} y^{-1} (Draved Mose; Clymo 1984), 6.5×10^{-5} to 5.5×10^{-4} y^{-1} (5 Scandinavian profiles; Clymo 1984), and 5.0×10^{-4} y^{-1} for a Finnish bog.

Although there are comments in the literature referring to 'a drop' in decay on traversing downwards through the peat profile, and

most workers have associated this with increasingly anoxic conditions, far fewer have attempted to quantify the drop. For example, Latter & Cragg (1967) noted a drop in the rate of loss of elements in the H horizon (-10 cm downwards), which apparently corresponded to the zone where waterlogging and reduced aeration frequently occurred. In 1967, Latter, Cragg & Heal reported that decomposition of cellophane and cotton strips began at the surface and 'stopped' at between -5 and -14 cm, depending on the site. However, some quantitative data do exist. Clymo (1965) recorded a decrease in the ratio 13:9:2 in the rate of dry weight loss of *Sphagnum* material from litter bags buried at the surface, at the depth of the water table and at -75 cm, respectively. Heal, Latter & Howson (1978), working on the blanket bog at MH, found that the same substrate showed a variation in decay of between 2.5x and 10x between the surface and -25 cm, and noted that other peat bog sites as far apart as Sweden, Ireland and Canada showed similar patterns. They attributed the variation to species and depth. In their model of 1967, Gore & Olson predicted constant fraction loss rates of 0.07 y^{-1} for the acrotelm and between 0.001 and 0.003 y^{-1} for the catotelm, and in 1978 the model constructed by Jones & Gore estimated a decrease in the decay rate of 0.065 for each centimetre of the profile traversed from the surface downwards. There are other quantified records of the sub-surface change in decay rate, too (e.g. Heal *et al* 1974; Tolonen, Davis & Widoff 1985). Most seem to suggest a maximum anaerobic rate of 10^{-3} y^{-1} compared with 10^{-8} y^{-1} arrived at in this study. There may be a number of (methodological) reasons for this. One contributory factor may be the depth interval over which the measurements were made. It is noticeable that where data from a complete peat profile are used (and this to date has meant age-bulk density data) they predict a lower value of α_c than when data relating to only the top 20 or 30 cm are used. It is true that there is commonly a sudden, significant drop in decay rate on passing from the acrotelm to the catotelm, but what little evidence there is suggests that the decay rate continues to decrease below this level, albeit at a much lower rate (see, for example, Heal *et al* 1974 and Tolonen, Davis & Widoff 1985). Given that the lower rates operate over 10-20x the depth of the (uppermost) 'anaerobic' zone commonly included in

data sets, this may result in something of an overestimate of α_c from such methods. Next, litter bag techniques suffer from technical drawbacks in the present context in that the nature of the material buried in them has a significant effect on the results obtained, insofar as freshly-dead plant material is known to decay relatively rapidly initially and then more slowly once the leachable and easily-metabolised material has been lost from it. Hence, studies which run for one or two seasons and which employ plant litter will probably overestimate decay, including that in the catotelm. This effect is compounded when freshly-dead material is introduced into the catotelm, where the natural material is more refractory. Thirdly, the use of standard materials such as pure cellulose or cellophane in the decomposition system introduces a foreign substance, so that the results from such studies can only be used as indicators of *relative* decay rates. The microbial population at the bottom end of the strip (commonly 20 cm or so long) will be presented with exactly the same quality of substrate as that above. In the normal course of events much of the readily-metabolised material will have been removed from organic matter lying at a depth of -20 cm. Thus under natural conditions the difference in the decay rate at -20 cm relative to that at the surface would be greater than will be indicated by the difference in weight loss from a uniform material at those same depths. This will lead to an overestimate of the decay rate towards the lower end of the strip.

It should be remembered that the values of α_c as calculated here are minimum estimates, since they do not take into account loss of carbon in methane bubbles (theoretically, all CO_2-C produced can dissolve) which, as discussed above, is probably considerable. The independent estimates of the anaerobic decay rate are not necessarily as inconsistent with those of the present study as they might at first appear.

5.6 DECAY IN THE ACROTELM

a) Calculation and evaluation of the aerobic decay rate, α_a

The decay rate in the acrotelm (α_a) is arrived at by comparing the net carbon flux from the acrotelm with the corresponding bulk

density value. The net carbon flux from the acrotelm is evaluated according to the following equation:

$$R_a = (R_a + R_c) - R_c \qquad (12)$$

where R_a and R_c represent the net carbon flux from the acrotelm and catotelm, respectively. Thus (R_a + R_c) represents the total carbon loss from the system as measured by the surface efflux. The choice of exactly what surface flux value to use depends on a number of factors. It is instructive to calculate α_a based on a number of different surface flux values, derived for different data sets and according to different assumptions, and to compare the results obtained. The emboldened values in Table 6.1a-e give the daily surface gas flux from 1 m^2 of bog at MH and CR. Total carbon flux is thus calculated to be between about 210 and 320 mg m^{-2} d^{-1} at MH, and about 500 mg m^{-2} d^{-1} at CR. The calculated values correspond to annual fluxes of 7.8, 11.8 and 18.3 mg cm^{-2} y^{-1} C, respectively. If the same calculations are applied to the gas flux data of Clymo & Reddaway (1971), also collected from the Burnt Hill pool-hummock complex (green mater removed), the corresponding values are between 4.6 and 5.1 mg cm^{-2} y^{-1} total carbon. Svensson (1980) reports 7.9 mg cm^{-2} y^{-1} for the acid mire at Stordalen. Other reports in the literature on methane emissions from acid peatlands give results for different plant communities but without any information about the proportional cover for each, or they report methane evolution per unit *volume* of peat, and most do not give information about simultaneous carbon dioxide evolution rates. Hence the two studies reported above are the only ones available at present with which total carbon fluxes from the general peatland surface may be compared. A more detailed comparison of CH_4-C and CO_2-C surface fluxes between this study and others will be made in the following chapter.

A working value of α_c has been determined above (3.9×10^{-5} y^{-1}) for the body of peat lying at or below -50 cm depth. If we now assume that this decay rate operates throughout the rest of the catotelm, up to an acrotelm-catotelm boundary at -15 cm (the choice of -15 cm for the depth of the acrotelm is explained below), we can calculate the

mass of carbon in the catotelm, and, using α_c, the flux. The mean total depths of peat at MH and CR were estimated from the arithmetic mean depths of the sampling sites at each location, giving a mean total depth of 320 cm at MH and 360 cm at CR, and respective catotelm depths of 305 cm and 345 cm. The mean bulk density at MH and CR, respectively, was calculated to be 0.037 g cm^{-3} and 0.033 g cm^{-3} (as carbon, calculated from the bulk density data used in Fig. 2.4). The mass of carbon in the catotelm is therefore about 11.3 g cm^{-2} at MH and 11.4 g cm^{-2} at CR, and, multiplying by the decay rate of 3.9 x 10^{-5} y^{-1}, the respective carbon fluxes from MH and CR catotelms (R_c) are 0.4 mg cm^{-2} y^{-1} and 0.4 mg cm^{-2} y^{-1}. Substituting into equation (12) we arrive at a net carbon efflux from the acrotelm, R_a, of between 7.4 mg cm^{-2} y^{-1} and 11.4 mg cm^{-2} y^{-1} at MH, and of 17.9 mg cm^{-2} y^{-1} at CR. These figures may be compared with corresponding figures of 7.8, 11.8 and 18.3 mg cm^{-2} y^{-1} for the total carbon flux. Thus the acrotelm would appear to be responsible for between 95% and 98% of the carbon lost from the profile each year, on this basis. In practice, the relative contributions will be affected by losses attributable to mass flow in solution or bubbles, or both, from the two layers.

To arrive at the decay rate for the acrotelm we now need to compare the carbon efflux from that region of the peat with the mass, which represents the carbon available for decay. If the assumption of a 15 cm-deep acrotelm is continued, the (carbon) bulk density is calculated as 13.1 mg cm^{-3} at MH and 13.7 mg cm^{-3} at CR, and the corresponding carbon mass 197 mg cm^{-2} and 206 mg cm^{-2}. Thus, the decay rate in the acrotelm is between 0.038 and 0.058 y^{-1} at MH and is 0.087 y^{-1} at CR. When compared with the α_c value of 3.9 x 10^{-5} y^{-1} arrived at above, these rates suggest about a one thousand-fold drop in decay rate on passing from the acrotelm to the catotelm at MH and CR. Thus, the rates of decay calculated from *in situ* measurements of gas concentration and surface flux are in agreement with other reports in the literature suggesting a several-fold drop in decay rate on passing from the acrotelm to the underlying waterlogged peat. The acrotelm decay rate calculated here, arrived at by a quite independent method from those previously adopted, may now be compared with those

other estimates. Jones & Gore (1978) gave a range of values between 0.022 and 0.185 y^{-1}, the differences being attributed to differing methodology and different substrate types. They considered a value of 0.07 y^{-1} to be a reasonable representation of surface decay rate. Clymo (1978) reported values of 0.032 to 0.062 y^{-1} for a *Sphagnum magellanicum* lawn at Burnt Hill, the exact rate depending again on the method used. In the same paper Clymo notes a decay rate for the IBP Abisko peatland site of 0.03 y^{-1}. Flanagan & Veum (1974) give values for the coastal tundra at Barrow, Alaska, of 0.05 - 0.09 y^{-1}, noting that this does not include losses from root respiration. Some reported values are somewhat higher; Heal *et al* (1981) report first-year losses (i.e. maximal) of 0.17 y^{-1} for a wet meadow site at Hardangervidda in Norway, and Berg, Kärenlampi & Veum (1975) report 0.24 y^{-1} losses for the first year from pulp cellulose in litter bags buried at -10 cm at Stordalen. These higher decay rates seem to be associated either with losses from freshly-dead material in the first season or two, or with those from 'foreign', more easily decayed, substrates. In both cases we would expect the resultant values to overestimate somewhat the true decay rate (see above). Thus a comparison of the estimates from the different methods is encouraging; those arrived at here for MH are very similar to field-measured rates at MH and other comparable sites, and the CR value is also very similar, lying more towards the top end of the range of values reported, if those possibly representing an overestimate of the true rate are disregarded.

5.7 DECAY AND ACCUMULATION IN THE TOTAL SYSTEM

a) Model predictions based on data from this study

In considering the peat accumulation model described in Chapter 1, a number of assumptions and consequences of the model became apparent which might not otherwise be obvious from a contemplation of the processes involved in peat bog formation on a purely descriptive basis. One of these, that decay continues in deep, anoxic peat, has been confirmed above, and now it has also been established, in line with one of the model's assumptions, that the anaerobic decay rate is indeed two or more orders of magnitude lower

than that in the acrotelm. One of the important conclusions reached from the theoretical considerations in Chapter 1 was that, although the anaerobic decay rate was very low, it was nonetheless very important, and indeed that it was precisely *because* of such a low decay rate that peat accumulates to the extent it does.

Table 5.4 gives the results of calculations to show examples of absolute and proportional carbon losses from the acrotelm and the catotelm on an annual basis. The values for α_a at MH and CR, and for α_c are those arrived at above. The mean total peat depth of each Site is taken as the arithmetic mean of the sampling site depths, and mean bulk densities are calculated from the data used to produce Fig. 2.4. In the first set of calculations the 'catotelm' is taken to be the peat at and below -15 cm depth; in the second set it is redefined as the peat at and below -25 cm. The third and fourth set of calculations impose theoretical changes in total peat depth and α_a, respectively, at MH in order to assess the proportional contributions of the catotelm to total carbon loss. The results clearly illustrate a number of points.

The contribution to total carbon loss made by the catotelm compared to that made by the acrotelm does not fall at the same rate as the corresponding drop in decay rate. This is a consequence of the larger volume of peat which is subject to anaerobic decay compared to the relatively small volume of the acrotelm in which the higher decay rate operates. Because of the very low decay rate in the catotelm, a change in the depth of the catotelm has a smaller effect on the absolute and relative contribution it makes to the total carbon losses than does a similar change in the depth of the acrotelm. Thus, an increase of 40 cm in the MH catotelm depth makes very little difference, but an increase in the acrotelm depth of just 10 cm almost doubles the amount of carbon lost from that portion of the peat and results in only about 60% of the original (proportional) catotelm contribution. This clearly illustrates the importance of the acrotelm depth and the low catotelm decay rate, since the first determines the amount of material remaining to enter the catotelm, and the second determines how much of this will decay. The lower α_c, the more peat will accumulate, all else being equal. This is so *despite* a very

small absolute value. Hence, for a given total depth of peat and a constant acrotelm depth and catotelm decay rate, the proportional contribution which the catotelm makes to the total carbon loss is

TABLE 5.4 Annual mass of carbon lost from the acrotelm and catotelm.

Summary calculations to illustrate the effect of a change in acrotelm depth, total peat depth, anaerobic decay rate and aerobic decay rate on annual carbon losses from the two parts of the system. The Table shows the amount of carbon lost per year.

Notes
Parameter values used in initial (case a) calculations.

Mean total peat depth (Z) : Z_{MH} 320 cm
Z_{CR} 360 cm
Acrotelm depth (Z_a) : 15 cm
Mean bulk density (ρ) : MH 0-15 cm 13.1 mg cm^{-3} C
> 15 cm 37.0 mg cm^{-3} C
CR 0-15 cm 13.7 mg cm^{-3} C
> 15 cm 33.0 mg cm^{-3} C
Acrotelm decay rate (α_a) : MH_i 0.033 y^{-1}
MH_{ii} 0.053 y^{-1}
CR 0.082 y^{-1}
Catotelm decay rate (α_c) : 1.16 x 10^{-4} y^{-1}

a) Initial parameter values as above

	Absolute losses (mg cm^{-2} y^{-1} C)		Proportional losses (%)	
	Acrotelm	Catotelm	C/(C+A)	C/A
MH_i	6.48	1.31	16.8	20.2
MH_{ii}	10.41	1.31	11.2	12.6
CR	16.85	1.32	7.3	7.8

b) Z_a = 25 cm

MH_i	10.81	1.27	10.5	11.7
MH_{ii}	17.36	1.27	6.8	7.3
CR	28.09	1.28	4.4	4.6

c) Z_{MH} = 360 cm; Z_a = 15 cm

MH_i	6.48	1.48	18.6	22.9
MH_{ii}	10.41	1.48	12.4	14.2

d) Z_{MH} = 320 cm; Z_a = 15 cm; α_a = 0.082 y^{-1}

MH	16.11	1.31	7.5	8.13

itself inversely related to the decay rate in the acrotelm. A reduction in the depth of the acrotelm results in a higher proportional (and absolute) contribution to carbon loss from the catotelm. Paradoxically, an increase in the total depth of peat (effectively of the *catotelm*) has a far smaller effect on the proportional contribution to carbon losses of the catotelm than does a change in the decay rate in the *acrotelm*. Imposing a theoretical increase in the total peat depth of 12.5% from 320 cm to 360 cm at MH resulted in very little change in proportional carbon losses, but comparing these results with those from CR calculations, in which all conditions were equal except for a higher decay rate in the acrotelm at CR, showed an increase in the proportional losses from the catotelm in an inverse ratio to the acrotelm decay rate operating. These results lead to the conclusion, in agreement with the theoretical considerations of Clymo (1984), that the depth of the acrotelm is important in the peat accumulation process since the deeper it is, the larger the volume of peat in which the higher decay rates will operate, and hence the smaller the proportion of original material which will survive to be incorporated later into the catotelm. Since decay proceeds so much more slowly in the catotelm, the amount of material entering that domain, itself a result of the depth of the acrotelm (and hence the time material is there and subject to faster decay), has a direct effect on the potential for peat accumulation, and its limits.

If the depth (mass) of the acrotelm is assumed to be constant, the amount of material passing annually from the acrotelm into the catotelm, denoted by p_c, the 'productivity' of the catotelm, can be calculated from the following equation:

$$p_c = p_a - \alpha_a m_a \quad g\ m^{-2}\ y^{-1} \qquad (13)$$

where p_a is the productivity of the acrotelm ($g\ m^{-2}\ y^{-1}$), α_a is the decay rate for the acrotelm (y^{-1}) and m_a is the mass in the acrotelm ($g\ m^{-2}$) which is obtained from the depth and bulk density. Although there have been detailed studies on productivity (e.g Chapman 1965; Clymo 1970; Clymo & Reddaway 1971; Forrest 1971 and Forrest & Smith

1975), none of the measurements correspond exactly to what is required here. Considering the figures available and the species and sites to which they apply, values of 300 g m^{-2} y^{-1} productivity for the Burnt Hill bog surface (wet, acid) and 600 g m^{-2} y^{-1} for Coom Rigg seem reasonable as working figures for the calculations which follow. These correspond to a carbon input of 120 and 240 g m^{-2} y^{-1}, respectively. Since we are concerned here with the effect of acrotelm depth, we need to pay careful attention to the choice of which value to use. The strict definition of the extent of the acrotelm which is usually accepted is that depth which corresponds to the position of the summer mean minimum water table (Ivanov 1981, cited by Clymo 1984). Water level measurements for the present study were not continuous, and the data collected are not suitable for the present purpose since, although they apply mainly to the summer months, they do not necessarily reflect mean minimum levels. A better indication of this is probably obtained from the physical and microbiological peat profile, since the acrotelm-catotelm boundary is closely associated with the visual characteristics of the peat which develop as a result of the extent of waterlogging they experience. Taking into consideration a number of descriptions of various characteristics of MH peat profiles in the literature (coloured horizons and microbial populations (Collins, D'Sylva & Latter 1978), bulk density changes, and redox potential profiles (Urquhart & Gore 1973), and Smith (undated), for example), a depth of -15 cm seems reasonable. This depth generally lies within the green-brown peat horizon, and close to the position of the minimum redox potential, a peak in facultative anaerobic bacteria numbers and bulk density, and where sulphide concentration increases. It may be slightly too deep for the Sites investigated in the present study, especially MH, to judge from the water level plots in Figs. 4.14 and 4.15, but 15 cm is a reasonable working figure with which to proceed. Over the top 15 cm of peat at the MH and CR sites, the mean bulk density (g C) was 0.012 g cm^{-3} (≡ 0.03 g cm^{-3} CH_2O) and 0.016 g cm^{-3} (≡ 0.04 g cm^{-3} CH_2O), respectively, giving m_a equal to 0.18 g cm^{-2}, and 0.24 g cm^{-2}. Using the values of α_a for MH and CR as above, $\alpha_a m_a$ evaluates to 0.007 g cm^{-2} y^{-1}, 0.010 g cm^{-2} y^{-1} and 0.021 g cm^{-2} y^{-1} for the two MH estimates and CR,

respectively. Subtracting these in turn from the acrotelm productivity value (p_a; MH 0.012 g cm^{-2} y^{-1} C (≡ 300 g m^{-2} y^{-1} CH_2O; CR 0.024 g cm^{-2} y^{-1} C) gives p_c as 5 x 10^{-3}, 2 x 10^{-3} and 3 x 10^{-3} g cm^{-2} y^{-1}, as carbon. These may be compared with (recalculated) values in Clymo (1984) of between 1.4 x 10^{-3} and 3.1 x 10^{-3} g cm^{-2} y^{-1} C for the five Scandinavian profiles (see Chapter 1 for details), and 2.1 x 10^{-3} g cm^{-2} y^{-1} C from data in Aaby & Tauber (1975) for another Scandinavian profile. The values from the present study are equivalent to 42% and 17% of p_a at MH and 13% at CR (cf 10% for a southern Finnish bog estimated by Clymo (1984)). It is necessary to obtain more accurate, specific, data by which to evaluate p_c.

5.8 SUMMARY

The quantitative results obtained from CH_4 and CO_2 measurements of MH and CR blanket peat have allowed an independent validation of an exponential decay model through comparison of measured gas concentration profiles and of derived parameter values with those predicted. In particular, the notion that decay continues, albeit at a very slow rate, throughout the catotelm, is upheld by the results. Measured values for the anaerobic decay rate accord very well with the few previously estimated by other methods. Following the validation, the current data have been used in the model to look further at the processes involved in peat decay and accumulation, and in particular to calculate the (minimum) rate at which methane and carbon dioxide are produced in deep peat. The likely consequences of the findings have been considered.

In order to proceed further with the model validation, and to improve the model, there is a need to determine the extent of carbon losses by other means than diffusion. In particular, losses in (methane) bubbles are probably highly significant, and their contribution must be quantified.

The mathematical description of peat decay is only one part of a peat accumulation model, already fairly advanced in its formulation. To refine the fuller model, it will be necessary to obtain more exact information about the transition between acrotelm and catotelm; for

example, the depth of the transition zone, its characteristics and seasonal variation. Such information will be needed to determine an accurate value of acrotelm depth (mass). Despite the numerous, detailed, productivity studies which have been undertaken, including those for MH, there remains a need for more, specifically designed to provide accurate information about small-area productivity which can be related directly to concomitant carbon losses over the same area (and underlying peat profile). The need arises because evaluation of p_c relies on calculating the difference between two very similar values, so the variables involved (p_a, α_a, m_a) must be accurately known. When such data are available it will be possible to continue with the validation process and refine mathematical (theoretical) descriptions of the peat accumulation process and the controlling factors which are presently operating. For the present, the availability of field-measured parameter values lags behind the theoretical considerations, and hampers further realistic model refinement.

CHAPTER 6

QUALITATIVE DISCUSSION

... whether you arrive at your destination or whether you reach somewhere else, or whether you never get anywhere at all, you're always busy, and you never do anything in particular; and when you've done it there's always something else to do ...

Kenneth Grahame, *The Wind in the Willows*

QUALITATIVE DISCUSSION

6.1 INTRODUCTION

Selected peat characteristics were recorded to help put more detail on the general descriptions of factors believed to have a bearing on peat decay, and particularly on methane production. Results of previous work, based largely on field studies, suggested complex, inter-related effects, and particularly the importance of the degree of waterlogging and temperature. Later, microbiological studies on peat isolates suggested pH might also have a regulatory effect on methanogenesis, and indicated connections between the methanogenic microflora (carbon cycle) and sulphate-reducing bacteria (sulphur cycle).

6.2 PROFILE MAXIMA AND MINIMA

Analysis of all the physico-chemical peat characteristics measured in this study confirmed the general view that most changes occur in the shallow horizons of the peat and that any changes below this tend to be gradual and relatively small. The results also indicated, more often than not, a point of inflexion on the profiles between about -20 cm and -50 cm; the resolution necessarily being coarse as a result of sample spacing designed to relate as far as possible to that of the gas samplers. The existence of these maxima and minima are not always convincing, or even apparent, from profile plots of the characteristics; sometimes they were only evident from fairly detailed, though straightforward, depth-class analyses, usually involving analysis of depths from the top down *and* from the bottom up (compare, for example, Figs. 4.61, 4.66 and 4.71 with Table 4.57).

It seems apparent that in freshwater sediments and peat (i.e. anoxic, sulphate-limited environments) there are maxima in microbiological activity near the surface. Also, predictions made from gas *concentration* profiles, which include a diffusion element, predict a peak in gas *production* below the surface (see Chapter 5). Note that the shape of the production and concentration profiles is not the same. This is also reported by Svensson & Rosswall (1984) in Stordalen peat and by Williams & Crawford (1984) in acid Minnesota

peat. Another important distinction to make is that between microbial (here, specifically bacterial) numbers and activity. Cappenberg (1974a) found that the depth of the maximum methane-producing bacterial population in freshwater Lake Vechten sediments apparently coincided with that of maximum CH_4 production (3-6 cm), but this is not always the case (e.g. Williams & Crawford (1984); acid peat).

It now seems beyond doubt that as the anoxic profile is traversed downwards, redox potential decreases (eg. Urquhart & Gore 1973; Heal, Latter & Howson 1978), and with it usually the total number of both aerobic and anaerobic micro-organisms. Aerobic respiration is replaced by anaerobic energy-releasing processes such as sulphate reduction and methane production. However, within such generalisations a wealth of processes are at work which are characteristic of not only the system concerned, but of the suite of immediately local conditions. Such small-scale variation makes further generalisation difficult.

As sulphate-reducers are obligate anaerobes, it is reasonable to assume that any significant metabolic activity of theirs will be restricted by the position of the water table and indicated by the redox potential. Indeed, Collins, D'Sylva & Latter (1978) found the maximum sulphate-reducing bacteria population between -5 and -20 cm (dark brown and green-brown horizons, MH). The green-brown horizon at MH (-10 to -19 cm) was found to correspond with the zone within which the water level fluctuated, and was roughly the position of the minimum redox potential. Dunican & Rosswall (1974) cite Siwasin (1971) as having recorded the highest density of obligate anaerobes in the green-brown horizon (there, -10 to -24 cm).

The silvered strip technique detected sulphide concentrations of 32 ppm, or more (≤ pS 5). Using the strips to detect the onset of a 'sulphide zone' it was clear that such a zone is closely related to that of the water level, usually beginning a few centimetres below it. Water level accounted for between 67% (MH) and 87% (CR) of variation in the depth of the upper limit of the sulphide zone. Hence, in general, sulphate-reducer activity is restricted to the waterlogged peat below the water table, but some results indicated that it may

occur in water-saturated micro-sites above this, within the zone of fluctuating water level and the capillary fringe.

It is convenient to consider here the redox potential profiles, in the context of the sulphide zone.

In accordance with all reports of redox potential measurements made *in situ*, those of the present study indicated dynamic potentials, varying with season and depth, and over small distances in the peat. Interpretation of redox values is notoriously difficult, since they reflect only the general oxidation-reduction state of the substrate, and do not in themselves give information about the nature of the processes giving rise to them (e.g. Whitfield 1969).

Absolute redox potential minima at MH were found between -10 cm and -50 cm, with minimum mean values between -25 cm and -50 cm. This is in broad agreement with Urquhart & Gore (1973). At MH, the onset of humified peat and the mean water level corresponded, at about -10 cm at MH, as far as these can be measured with any accuracy (Fig. 4.73). The mean minimum redox potential was thus apparently *below* the level at which the water level fluctuated (cf Heal, Latter & Howson 1978, above). Minima at CR were recorded at between -1 and -2 m in both study years. It is difficult to accept this in the light of so many other results suggesting a minimum potential to be common in the top 50 cm of peat (or freshwater sediment). However, the result could be explained if a minimum occurred at CR below about -25 cm. If this were the case, it would have fallen in the zone of peat consistently not sampled, that is, between the deepest peat block sample and the uppermost core sample.

Whilst the silvered strip method is essentially an all-or-nothing technique, the total sulphide concentration data provide quantitative information about the activity of sulphate-reducing bacteria.

Redox potential was the single most important (significant) factor correlated with sulphide concentration. Maximum sulphide concentration coincided in position with minimum redox potential. The maximum concentration in the top 25 cm occurred at about -20 cm. Sulphide concentration maxima moved downwards at a rate of approximately 20 cm per month (strictly, per interval between field visits), over the top 20 cm. Calculations (Section 4.1.2, Weather

Record - Peat temperature) predict a time lag for temperature of about a month between the surface and -20 cm, and about 10 weeks between the surface and -50 cm. This suggests a direct (inverse) relationship between redox potential and sulphide concentration, and implies a common (microbial) mediator which is temperature-dependent. However, the situation is not necessarily so simple, since the respective maxima and minima do not coincide temporally, apparently, (though it should be remembered that different areas of peat were sampled on different visits). In the top 10-20 cm the (June) minimum sulphide concentration lagged one 'month' behind the maximum redox potential and, conversely, the maximum concentration occurred one 'month' behind the August redox potential minimum. At depths of more than 1 m the timing of the respective maxima and minima coincided. If such lags at the surface are real, they suggest that the redox potential is initially lowered by a population of anaerobic micro-organisms which are temperature-dependent, but which do not produce sulphide. Later, perhaps once the redox potential has reached a critical level such that sulphate-reducing bacteria can operate, they too are able to respond to the increase in temperature. Put another way, the sulphate-reducers may be outcompeted for available substrate initially, and can only predominate at redox potentials low enough to give them an advantage in metabolising more reduced substrates or substrates which yield low energies. It may be that this 'other' anaerobic population is one of sulphate-reducers which respond to higher temperatures initially, or first, by reducing substrates such as acetate or lactate to carbon dioxide and hydrogen (see Appendix M). This hydrogen may then provide the means for the same, or other, sulphate-reducing bacteria to produce H_2S.

The lack of any lag time between redox minima and sulphide maxima deeper in the peat may be explained if it is assumed that the more oxidised substrates are largely exhausted at those depths, such that there is no significant competition for sulphate-reducers.

Redox potential falls as electron acceptors are used up (reduced). Hence, it seems probable that seasonal redox changes in shallow (<50 cm) peat are the result of changes in peat chemistry mediated by the temperature responses of microbial metabolism. They

indicate a maximum (microbial) metabolic activity commonly between -25 cm and -50 cm. If the above interpretation of results is correct, it follows that as the peat is warmed from above in spring, metabolic activity will increase in line with the temperature rise, all else being equal, and the redox potential will fall. Thus the minimum potential will move upwards in warm weather and sink deeper below the surface in cold. The present results indicate precisely such a movement of redox minima (Fig. 4.66). Furthermore, they show a highly significant ($p<0.001$) seasonal effect at all depths (with the greatest changes in the top 50 cm). The occurrence of seasonal changes to the base of the peat suggests that temperature is probably not the sole driving force for the changes. Since they are correlated with sulphide concentration, such seasonal changes in redox potential could be expected to be reflected in seasonal movements of the sulphide zone. This was indeed so. The depth of the sulphide zone relative both to the peat surface and to the water level was seasonally variable (see Fig. 4.74). The divergence between water and sulphide zone level between November and April may be a result of the relative effects of seasonal temperature changes on production and diffusion (assuming diffusion to be greater than production in winter). The earlier divergence seen in the drier microhabitats suggests that diffusion increases over production in drier microhabitats (i.e. deeper in the peat) before it occurs near the surface. A full explanation of the divergence, and the differences between microhabitats, awaits a knowledge of the relative effects of temperature on H_2S production and diffusion in peat. We need results for temperature dependence for both processes over a range of temperatures relevant to the peat environment.

In the literature there is considerable attention given to the activities of methanogens, sulphate-reducing bacteria and their interactions. It used to be thought that the two groups were mutually exclusive in their activities; thermodynamic considerations indicate that methane production is less favourable energetically than is sulphate reduction, such that the two processes were thought to occur sequentially. It is certainly true that in sulphate-limited sediments (but where some sulphate is available) sulphate-reducing bacteria are

able to make use of the hydrogen generated by fermentation reactions (mediated by, for example, acetogenic bacteria and at least some sulphate-reducing bacteria themselves), and since the process of sulphate reduction to H_2S is more energetically favourable than the reduction of CO_2 to CH_4 (Bryant *et al* 1977), they are able to outcompete the methanogens for the hydrogen. However, there is now considerable evidence, mainly from freshwater sediment studies, for some overlap between the two processes such that methane-producing bacteria and sulphate-reducing bacteria not only occur within the same sediment zone, but may also be active simultaneously (Jakobsen, Patrick & Williams 1981; Smith & Klug 1981). Furthermore, it has now become clear that the range of substrates which may be used by the two groups, respectively, is wider than was once thought, and there are more links between their activities than was previously realised (Appendix M). For example, acetate, carbon dioxide and hydrogen are common substrates. The ability of either group to outcompete the other is dependent on the availability of electron acceptors and the reduced organic substrates it is able to utilise. For example, although thermodynamics predicts that sulphate-reducing bacteria can outcompete methanogens for hydrogen, this relates only to the situation where sulphate is available as electron acceptor. When sulphate is not available, the sulphate-reducing bacteria are unable to utilise the hydrogen, which then becomes available to the methanogens. Hence the active pathways for electron and carbon flow depend on the availability of utilisable substrates and electron acceptors for each group, and these may change seasonally and with depth (Jones & Simon 1985, and this study). The interrelations of the groups, therefore, will also be likely to change with season and sediment horizon, and it now seems clear that whilst the two are indeed in competition for substrates such as H_2, under certain conditions, at other times they *provide* the other with substrate (e.g. H_2 or acetate may be provided to a methanogen by a sulphate-reducer). Thus the two operate very closely, and although the various conditions in the sediment will favour the activities of one over the other and thus tend to support one or other as the dominant, there will also be regions of the sediment where conditions are conducive to their co-

existence. Incidentally, the distinction may often simply be a matter of the scale (size of environment) being considered.

It was established above that sulphide concentration is inversely correlated with redox potential. In the same analyses, sulphide concentration increased with a decrease in temperature (the median interface temperature for the period since the previous field visit). This appears to be a contradiction of the inference so far of a directly temperature-dependent sulphate-reducer population. If the peat water were saturated with H_2S, the apparent paradox might be explained by the reduction in H_2S solubility with warming. Thus, if the physical temperature effects were greater than the biological ones, an increase in temperature would result in a decrease in the measured sulphide concentration. However, only about 2% of samples showed a saturated solution.

A similar 'physical vs biological' case might be made to explain the seasonal movement of the sulphide concentration maxima and minima within the profile. The surface concentration perhaps builds up in winter as a result of slowed diffusion rather than increased metabolic activity.

To explain the negative relationship between temperature and sulphide concentration, and also the surface sulphide concentration maximum at cooler times of the year, it has been argued that at cooler times diffusion may be slowed more than microbial activity, thus creating an accumulation of sulphide. But it has also been argued, above, to explain the seasonal movement of the upper limit of the sulphide zone, that in winter the fall in microbial activity is relatively large compared to that of diffusion, so that any accumulated sulphide is lost faster than it is replenished. Clearly, an accurate description of the reasons for the changes in distribution of sulphide must take into account the relative effect of temperature on biological (microbial activity) and physical (diffusion and solubility) processes (and also the effect of chemical oxidation of sulphide to sulphate).

It is evident, then, that changes in the shape of profiles of microbial (density and) activity, and substrate/product concentrations in sediments are the integrated result of many complex processes.

6.3 RELATIONSHIP BETWEEN PEAT CHARACTERISTICS AND GAS CONCENTRATIONS

Regression analyses designed to clarify any relationships between peat physico-chemical characteristics and methane and carbon dioxide concentrations returned low r^2 values and high probability levels, in the main. Chemical properties of the profile (as measured by redox potential, pH and pS) accounted for less than 8% of the variation in CH_4-C concentration; including the best temperature variable in the regressions increased the r^2 value to between 0.21 (N_2-filled sampler data) and 0.36 (air-filled). The comparable regression analyses for CO_2-C concentration were yet less revealing; the best multiple regression equation relating CO_2-C concentration to the three chemical properties accounted for only 7% of the variation ($p < 0.01$), and including a temperature variable had no effect. Indeed, overall, no consistent pattern was revealed by the regression analyses which might help to interpret the causes of variation in CH_4-C and CO_2-C concentrations over the whole profile. Variation in causality (and association) occurred with site, depth, date and whether air or N_2 had been used to fill the samplers. The lack of correspondence between 'replicate' CH_4-C concentrations and 'replicate' CO_2-C concentrations at all depths at MH, compared with the non-significant site effect obtained for CR, suggests an inherent complexity which will require much further, careful, research to unravel.

Some improvement might have resulted from a non-linear regression approach, but the amount of data did not justify the use of extra parameters.

Notwithstanding the unhelpful results of the regression analyses, a number of effects were suggested. Further, there were consistencies which are worth bearing in mind since they will require further scrutiny in any attempt to understand more fully the production and distribution of peat gases.

It seems clear (see Figs. 4.53 and 4.55) that the overall profile maximum *concentration* of CH_4-C occurs higher up the profile, at between -2 m and -3 m, than does the maximum CO_2-C concentration (-3 m to -4 m). At the same time it is apparent (compare Tables 5.1 and 5.2) that the depth of maximum *production* of the gases differs a) from

that of *concentration*, and b) from each other. Maximum production of methane occurs at between -20 cm and -50 cm, whereas maximum production of carbon dioxide was at -20 cm. Production of both gases decreases down the profile (cf *concentration* profiles). Whereas methane is produced only under strictly anoxic conditions, carbon dioxide results from both aerobic and anaerobic processes. Peat at -50 cm will be permanently waterlogged and largely, if not totally, anoxic, whereas peat at -20 cm will probably be in the horizon of fluctuating water level, and will certainly experience fluctuating degrees of oxygenation, if not of waterlogging. Therefore, at -50 cm, all else being equal, methane can be formed continuously, whereas in shallower peat it is likely that the redox potential will rise periodically to prohibitive levels, whilst still allowing the production of carbon dioxide. Furthermore, since oxidation of CH_4-C generates carbon dioxide, the net difference in their rates of production over the top 50 cm of peat may be the result of methane produced deeper down being oxidised as it diffuses to the surface. This has been suggested to explain the results of those working on marine waters and sediments (for example, Barnes & Goldberg 1976; Reeburg 1976, 1980; Ward *et al* 1987). Whilst there is, of course, the complication of variation in microbial population size, the micro-organisms concerned are only able to metabolise under strictly anoxic conditions. We need more co-ordinated research designed to compare population size, activity, environmental variables and gas production rates simultaneously in the same peat (samples). However, at this stage it is interesting to note that the absolute annual S^{2-} concentration maxima were recorded between -25 cm and -50 cm, and in the top 25 cm the maxima occurred about 10 cm below the uppermost limit of the humified layer.

Another area of analysis which showed some consistency of results was the association between temperature and gas concentration (Tables 4.47 and 4.50). Peat temperature and methane concentration were negatively associated over the whole profile, though less so below -2 m when N_2 was used in the samplers, and the association was positive when air was used. Such relationships are not immediately obvious from a comparison of Figs. 4.53 and 4.55 with the predicted

temperature profiles for the top 1.5 m of peat shown in Fig. 4.11. There seems to be a lag of between one and two months between the peat temperature change and any noticeable effect in gas *concentration*. In contrast to the situation for CH_4-C concentration, that of CO_2-C was more closely (positively) associated with air temperature than with peat temperature, and the effect was much clearer when air was used to fill the sampler. This is consistent with an increase in aerobic activity (including methane oxidation?) with an increase in temperature. Peat temperature was also positively correlated with carbon dioxide concentration.

Of the peat characteristics measured, after temperature pH was the second most important in relation to CH_4-C concentration. In early considerations of peat accumulation it was considered that low pH was one of the main reasons for the low rates of microbial respiration (and hence decay). However, it became clear from the work of, for example, Clymo & Reddaway (1971), Svensson (see Svensson 1983 for references from 1973 onwards), and Harriss *et al* (1985), on temperate and subarctic peatlands, that despite the very low pH of ombrotrophic peat, significant amounts of methane were produced and lost from it annually. It now seems clear that methanogens are operating at sub-optimal pH in acid, ombrotrophic, peat (for example, see Cappenberg 1974a; Cappenberg 1975; Williams & Crawford 1984 and Yarrington & Wynn-Williams 1985).

Regression analyses for methane concentration on peat characteristics in the present study returned equal r^2 values for temperature and pH at depths between -0.2 m and -0.5 m at CR. Below -2 m pH accounted for between 7% ($p<0.01$) and 79% ($p<0.001$) of the variation in methane concentration. The thermal damping depth for these peats was calculated to be between -40 cm and -80 cm. Hence, at depths below this there will be only a small ($\simeq 6°C$) seasonal temperature fluctuation, and at -2 m and deeper, it is safe to assume that the peat remains at a nearly constant 5°C (the mean annual air temperature at MH and CR). Under such conditions, the effect of pH could conceivably be greater than that of temperature; indeed, the field pH profiles indicated more significant changes with depth, below

-1 m, than with season. The effect of pH on methane concentration at 5°C is assumed to be less than that for a similar shift in pH at higher temperatures, such as those experienced for half the year in the shallower peat, but in the shallower peat the effect of temperature apparently swamps that of pH, and becomes dominant. Yarrington & Wynn-Williams (1985) also found that temperature and pH effects on methanogenesis were interrelated, such that either could become rate-limiting.

As early as 1974 Svensson (cited in Svensson, Veum & Kjelvik 1975) reported an enhanced rate of methane *flux* from minerotrophic areas of Stordalen mire, compared with oligotrophic areas. Similar findings have been reported by a number of workers since (e.g. Svensson & Rosswall 1984). The unexpectedly high methane flux from site 17 (in the lagg adjacent to the conifer plantation) lends further support to the idea of some pH-dependence.

Any relationship between pH and *methanogenesis* profiles was not consistent.

The effectof pH on CO_2-C concentration was unclear.

6.4 FACTORS AFFECTING GAS FLUXES

Turning now from concentrations to fluxes, interesting comparisons may be made between the results obtained from garden and field peat. (Absolute fluxes from areas of intact ombrotrophic bog are considered below.) The 'annual' mean CH_4-C flux from the field sites was 17 mg m^{-2} d^{-1} (Uncut, Tables 4.9 and 4.13), compared with 35 mg m^{-2} d^{-1} in the garden (Table 4.25; mean of UP, UL and UH CH_4-C fluxes for all experimental stages together). These two figures are not strictly comparable for a number of reasons (e.g. field data not collected year-round; relative areas of different microhabitats not taken into account, assumed to be 1:1; water levels regulated in garden peat but fluctuated 'naturally' in field), but they clearly suggest a higher CH_4-C flux from the garden than from the field peat. Given that the garden peat originated from MH, the obvious explanation is the effect of a warmer régime, indicating the extent to which the low mean temperature in the field (5°C cf 12°C in the garden) is

probably checking methane efflux. That the increase in flux is due to a real increase in microbial activity and methane production is suggested by the similar seasonal flux pattern in the garden and field, and because if the higher temperatures in the garden caused an increase in diffusion greater than that in production, the increase in flux would probably not be sustainable.

There was no difference between MH and CR mean CH_4-C flux, despite different total peat depths, which supports the conclusion reached in the previous chapter: that most of the methane comes from the acrotelm.

A number of possibilities exist to explain the difference in CO_2-C flux from the MH and CR Sites. It is unlikely that the difference reflects simply the effect of temperature (due to altitude and exposure) on respiration and photosynthesis. A small difference may be due to differences in the relative amounts of photosynthetic : non-photosynthetic vegetation. However, carbon dioxide is released not only as a result of excess aerobic respiration over photosynthesis, but also by the oxidation of CH_4-C. Results of analyses of variance to detect any effect of total peat depth on methane flux suggested that there was no significant effect until peat of more than 3 m total depth was considered. The mean depth of peat at CR was 3.6 m. This may, then, go at least part way to explaining the difference between the mean flux quotient of CO_2 / CH_4. At CR the ratio was 16.4, compared with around 10 for MH and the garden cores. Methane oxidation may make a significant contribution to the absolute fluxes of CH_4-C and CO_2-C, and the balance between them. Temperature also has an effect, and, if the Q_{10} values for the respective micro-organisms were equal, this would be greater on the surface CO_2 production processes than on either (sub-surface) methane production or oxidation. Clearly there are many permutations of the likely processes involved which could explain the results. For this aspect of peat gas production studies also, we now need a more finely-tuned (field) experimental design, in connection with laboratory experiments to distinguish and describe the production and diffusion elements of the flux process.

6.5 POSSIBLE MODIFICATIONS TO ORIGINAL 'POINT SOURCE' GAS FLUXES

The variability of a range of peat characteristics over even small distances in the peat has frequently been commented upon. At MH the CH_4-C flux means varied three-fold over the three (surface sampling) sites (total peat depths ranged from 3.0 to 3.4 m), but the proportional range of CO_2-C efflux was less. Conversely, the mean CH_4-C flux from the three deepest CR sites (total peat depth 4.0 to 5.0 m) was remarkably similar (Table 4.13). These results appear to support the popular contention that deep peat is fairly homogeneous and that most variation is seen at shallow depths. This may be so, or, as was reasoned above, it may be that there are differences at depth, but that near-surface and surface processes modify the resulting variation in sub-surface production and flux (possibly according to physical laws). If so, it might be possible to argue that in shallower peat (total depth) the effects of variation in peat characteristics are more obvious, insofar as they may be more immediately manifested at the surface as a result of their proximity, and also the reduced residence time during which modification could occur.

The CO_2-C / CH_4-C quotients given above for CR, and for MH and the garden, suggest that deeper peat evolves relatively more CO_2-C than CH_4-C than does shallower. These quotients are overall means for the Sites, and reference to Table 4.13 does not lead to the same conclusion. Clearly, at CR at least, methane flux was considerably higher, and that of CO_2 much lower from the three deeper sites. Thus, *within* the CR Site, the CO_2-C : CH_4-C ratios were >40 for the two shallow sites (this, despite the unexpectedly high methane flux from site 17) and between 6 and 14 for the three deep sites. This fits with expectation. Indeed, it was because such an increased methane flux might occur over deeper peat that CR was chosen and the sampling régime so designed. The apparent discrepancy in the results may be due in part to differences in surface vegetation.

All green biomass was removed from one of each pair of replicate buckets in order to eliminate any variation in flux attributable to different biomass quantity and quality. As mentioned above, the

evolved carbon dioxide may not be due exclusively to aerobic respiration; a proportion of it may originate from oxidation of methane (aerobic, anaerobic or both). A number of the results are interesting in this respect. In all cut cores the most important temperature variable significantly correlated with CO_2-C efflux was the mean peat temperature since the previous sample, compared with intact cores where the air or interface temperature gave the best results. In accordance with the idea of two distinct sources of CO_2, the analysis of variance to investigate the HABITAT.CUT interaction on surface flux returned a non-significant result for CH_4 (strictly a sub-surface, anoxic, production) but was significant for CO_2. Such a contrast may be just a reflection of the microhabitat differences in surface vegetation and the effect of its removal on aerobic respiration (different absolute amounts removed, different ratio of photosynthetic : non-photosynthetic material), but, given the change in temperature variable significance on cutting, it may also include an element attributable to sub-surface production of CO_2.

There were numerous results which supported the idea that either the quality, quantity (or both) of surface vegetation also had an effect on the net flux of CH_4-C from the peat. Methane efflux was significantly reduced by removal of the green matter (Tables 4.9, 4.13 and 4.25) (which may also help to explain the concomitant reduction in carbon dioxide flux), and more restricted data sets than the complete set which yielded the non-significant HABITAT.CUT result for methane flux suggested that there were, in fact, differences in the effect of cutting on CH_4-C efflux between the three microhabitats. The non-significant HABITAT.CUT interaction reflects the inconsistency between the different microhabitat results. However, in support of the notion that the different microhabitats' surface vegetation may play a rôle in the difference in CH_4-C efflux, were the comparative results from the seven-variable regressions: MH and CR returned similar results for CH_4-C flux when cut area data were used, but differed when data from intact areas were used.

It could be argued that the reduction in CH_4-C flux (and that of CO_2-C) on removal of the green matter was an artefact caused by the increase in gas volume above the water tabke and the consequent

decrease in gas concentration. However, this is unlikely, since the differences were not consistent with time, and differed in amount between components. Furthermore, at MH, lawns showed the largest absolute reduction in CH_4-C flux, and the mean weight of green matter initially removed was 25 g, compared with 2 g from pools and 63 g from hummocks.

There was no direct correspondence between the extent of the reduction in CH_4-C flux and the weight of green matter removed (initial removal or at sampling). In the garden and at MH there was a decrease in the rate of CH_4-C flux reduction per unit dry weight of green matter initially removed on progressing from the wetter to the drier habitats, that is, removal of green matter had less of an effect per gram of biomass removed the drier the habitat. At CR there were four sites where the effect of cutting was significant, and each showed a very similar rate of decrease in flux of between 0.2 and 0.3 mg m^{-2} y^{-1} dry weight removed.

Finally, before moving away from surface vegetation effects, it should be noted that removal of the green matter may result in a *significant* reduction in flux (at MH the reduction in CH_4-C was 50% and at CR 63%, and the reduction in CO_2-C was 13% at MH and 43% at CR). It is important, therefore, to consider this when comparing results from different studies. Thus, in experiments and monitoring programmes concerned with *absolute* carbon losses and carbon budgets, it is important either to work with intact systems, or to be certain of the conversion factor necessary to convert 'cut' data into 'uncut'. The conversions are likely to be varied and complex, and there is much scope for research into the mechanisms involved. As early as 1966 Hartman & Brown found methane to be a constituent of the internal atmosphere of *Elodea canadensis* and *Myriophyllum exalbescens / Ceratophyllum demersum* (sic). Dacey & Klug (1979) reported that methane was conducted from a lake sediment through the lacunae of the water lily *Nuphar luteum* and via its emergent leaves to the atmosphere. They calculated that 46% of the CH_4 lost from the study lake was accounted for in this way. Thus it is plausible that some of the methane evolved from peat may reach the surface via the internal

tissues of some plants. It is not clear why cutting might reduce the effect of any such mechanism.

Fig. 6.1 offers a possible explanatiobn of the main trends in the results. For the purpose of simplification, it has been assumed that methane and carbon dioxide are *produced* at equivalent rates in the peat. The width of the arrows represents the mass of carbon. The bottom of the arrows represents the rate of gaseous carbon produciton as CH_4-C and CO_2-C, and the arrowhead the efflux of these gases from the bog surface. The width of the arrowheads is fixed by the measured flux (values from Table 4.29), and it is assumed that the peat is in equilibrium, so that production is equal to efflux. The diagram depicts a portion of the methane produced as being oxidised to CO_2 as it diffuses upwards to the peat surface. Thus the diagram illustrates the considerably greater total flux from hummocks compared with pools, but the smaller proportion, and absolute amount, of CH_4-C. Coupled with the assumption of equal CH_4-C and CO_2-C production, this leads to the conclusion that more (in absolute terms and relatively) methane is converted to carbon dioxide in hummocks, between its point of production and the peat surface, than in pools. When the green matter was removed from hummocks, the CH_4-C flux was reduced by 93% (Table 4.29), suggesting that anything up to 93% of the methane might be evolved via the surface vegetation. Thus, it is possible that the surface CH_4-C flux from hummocks represents only a fraction of the original methane production, and that a considerable proportion never reaches the surface as methane, but is oxidised to carbon dioxide as it diffuses upwards through the peat matrix. A contrasting situation seems likely to occur in pools, where methane does not have to run the gauntlet of an aerobic acrotelm, and reaches the surface directly from the waterlogged zone where it is produced (although there may be a limited, shallow, surface zone where oxygen concentrations are sufficiently high to inhibit methanogenesis). This would lead to a higher proportion of the original methane production being sampled at the surface, compared with carbon dioxide (and, apparently, higher absolute fluxes). Furthermore, plants are likely to play a less important rôle as escape routes for methane from pools than from hummocks (fewer of them and more direct peat surface efflux), so that

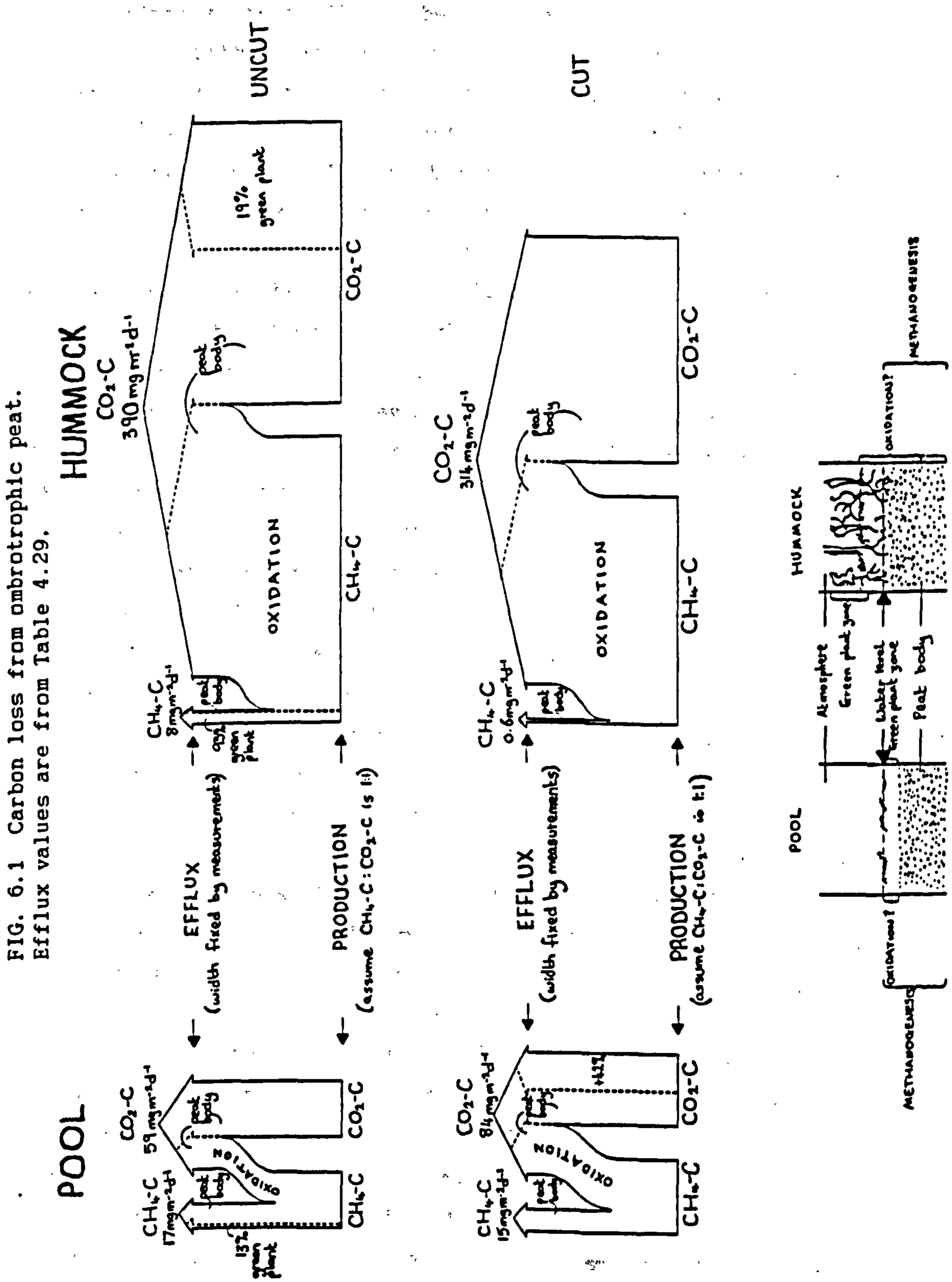


FIG. 6.1 Carbon loss from ombrotrophic peat.
Efflux values are from Table 4.29.

less of an effect (reduction) on flux would be expected when the green matter was removed. This is precisely what the results indicate: on cutting, hummock CH_4-C flux was reduced by 93%, that of pools by 13%. The diagrams in Fig. 6.1 include these proportions within the 'uncut' microhabitat arowheads, and are drawn as if no methane or carbon dioxide is lost via the cut plant tissues. However, as was noted above, this possibility cannot be ruled out. No attempt has been made to quantify this, and the 'cut' microhabitat arrows (except that for pool CO_2) omit a proportion marked 'plant'.

A considerably higher CO_2-C flux was measured over hummocks than over pools. Continuing the simplifying assumption that CO_2-C and CH_4-C are produced at roughly equal rates, and combining this with the fact that when the green matter was removed from the hummocks, CO_2-C flux was reduced by 19%, leads to the idea that much of the CO_2-C flux originates from oxidation of methane in the peat body, and reaches the surface via the peat. Some comes from living biomass respiration. Following on from this, it seems reasonable to suppose that the smaller absolute CO_2-C flux above pools arises from a relatively low rate of methane oxidation, and also from there being less respiring material in pools than on hummocks. Only the *respiratory* fraction of the CO_2-C flux is directly affected by removing the green matter. This may explain the larger absolute, and smaller relative, reduction of CO_2-C flux on removing the green matter from hummocks compared with lawns (Table 4.29).

Attempts to clarify any association (or influence) of water level and temperature with methane and carbon dioxide flux gave mixed results which suggested for both gases complex interactions which it was not possible to separate with confidence, and which themselves varied with microhabitat and season. In many cases methane flux began to increase before that of CO_2-C. The time lag appeared to be about a month, which again probably reflected the sampling interval rather than the true lag time. The difference may result from the effects of the spring temperature increase. As the peat warms from above, diffusion and dissolution may increase before the temperature is high enough for biological activity to begin. Thus stored gases will be evolved before new production (and its efflux) begins. Methane flux

will probably begin to increase first because of its higher concentration relative to its saturation concentration. Furthermore, although all methane is produced in the deeper (and in winter, warmer) regions of the peat, a portion of the carbon dioxide originates from surface processes which will be subject to extreme fluctuations in air temperature. These regions will reach a mean temperature which allows biological activity later than deeper, methanogenic, regions.

It is not surprising to find that temperature affects gas production and flux, but the extent of any direct association differed between microhabitats. In hummocks temperature was the single most important influence on CO_2-C flux, but this was not so for the other microhabitats. Water level clearly played a rôle in influencing the (significantly different) mean carbon fluxes from the three microhabitats (both CH_4-C and CO_2-C), but once the gross variation in water levels *between* microhabitats was removed, the effect of smaller differences *within* microhabitats on their flux was less clear, and was confounded with temperature effects. Consideration of all the results leads to the conclusion that peat temperature has a direct effect on its rate of movement (diffusion and mass flow) upwards from its source, to the surface vegetation and through that to the atmosphere above.

Once again, then, it is clear that we need to look more closely at the effects of temperature on both the production (biological) and movement (physical) of methane and carbon dioxide in peat. Similarly, there is a need for closer scrutiny of these same aspects with respect to the water level (and water content). And yet again, having clarified some of these relationships, then to understand and be able to describe how they interact. This, in addition to the need for studies on methane oxidation and the significance of plant tissue as an escape route for methane already noted above, will be needed in order to reach a point where we may be able to make confident predictions about gaseous carbon production and emission from peat.

Why peatlands should act as a sink for methane is not clear. In the present study and that of Harriss, Sebacher & Day (1982), a negative methane flux was recorded at intervals over 7-9 months of the year. It is possible that the negative fluxes reflect purely physical

processes, driven by a change in concentration gradient across the peat-air interface, but it is not obvious what might cause such a reversal. According to theoretical considerations (see Fig. 4.11), the periods when negative fluxes were recorded (April to January) do not coincide with any particular temperature profile; at some times the peat will be warmest at the surface and sometimes warmer at depth.

6.6 ABSOLUTE GAS FLUXES FROM INTEGRAL PEATLANDS

So far in the Discussion, consideration has been restricted to identifying and describing the effect of significant factors on the net flux of methane and carbon dioxide from blanket peat, that is, to mechanisms. Table 6.1 gives the integrated effects of the mechanisms over the peat bog as a whole; a summary of calculations based on the (net) surface fluxes measured during the study. Such information is of more immediate relevance when asking (quantitative) questions about carbon cycling and emissions from complete peatland ecosystems. The values in the Table are based on uncut area data, and include adjustments for the relative area of the microhabitats.

Total carbon flux was less (214-323 mg m^{-2} d^{-1} C) from MH blanket bog than from CR (496 mg m^{-2} d^{-1}), from sites of similar total peat depth. The exact flux varied by ± 50% according to what flux value was used for "general blanket bog" areas, which were not monitored. Interestingly, if all CR sites were included in the calculations (mean total peat depth 3.6 m), the figure was only 295 mg m^{-2} d^{-1} C. The MH figures may be compared directly with the results from the study of Clymo & Reddaway (1971), also on Burnt Hill. Their proportional microhabitat areas were slightly different (P : L : H : general blanket bog was 0.18 : 0.13 : 0.08 : 0.61, compared with 0.16 : 0.08 : 0.02 : 0.75 for this study), but the relative proportions were the same, and the flux is calculated to be 139 mg m^{-2} d^{-1} C. Their measurements were made on cut areas, and when adjusted for this (according to the effect of cutting shown in Table 4.9) the result is 165 mg m^{-2} d^{-1} C.

Since that first report of quantified methane and carbon dioxide flux from acid peat of Clymo & Reddaway, Svensson has published

TABLE 6.1 Carbon flux from balnket peat bogs. Summary of integrated carbon losses from the blanket peat at Moor House and Coom Rigg, comparing the proportion attributable to the different microhabitats present. Calculations are based on surface flux data from uncut sampling areas.

MOOR HOUSE

Proportional areas covered by each microhabitat on Burnt Hill study area were as follows: hummock 0.015; lawn 0.080; pool 0.160; general blanket bog 0.745. Flux values are taken from Table 4.29.

a) Assume the carbon flux from the general blanket bog is the same as that from hummocks.

Proportional flux from each microhabitat (m^{-2} d^{-1})

	CH_4-C (mg)	CO_2-C (mg)	Total C (mg)	Ratio CH_4-C: CO_2-C	Proportion CH_4-C (%)	Proportion CO_2-C (%)
UH	8.2	390	398.2	1:47.6	2.1	97.9
UL	25.1	80	105.1	1: 3.2	23.9	76.1
UP	17.1	59	76.1	1: 3.5	22.5	77.5
Ratio P:L:H	2.1:3.1:1	1:1.4:6.6	1:1.4:5.2			

Flux from Burnt Hill blanket bog (m^{-2} d^{-1})

	Area (%)	CH_4-C Absolute (mg)	CH_4-C Propn (mg)	CO_2-C Absolute (mg)	CO_2-C Propn (mg)	Total C (mg)
UH	76.0	8.2	6.23	390	296.4	302.63
UL	8.0	25.1	2.01	80	6.40	8.41
UP	16.0	17.1	2.74	59	9.44	12.18
Total	100.0		10.98		312.24	323.22

Flux ratios

	Proportional CH_4-C:CO_2-C	Proportion of total, per microhabitat CH_4-C (%)	Proportion of total, per microhabitat CO_2-C	Proportion of total over whole bog CH_4-C (%)	Proportion of total over whole bog CO_2-C
UH	1 : 47.6	2.1	97.9	1.9	91.7
UL	1 : 3.2	23.9	76.1	0.6	2.0
UP	1 : 3.4	22.5	77.5	0.9	2.9
Total				3.4	96.6

	CH_4-C	CO_2-C	Total
P:L:H	1.4 : 1 : 3.1	0.03 : 1 : 46.3	1.4 : 1 : 36.0

b) Assume the carbon flux from the general blanket bog (BB) is half the total of that from hummocks and lawns (i.e. (UH + UL)/2), since water level does affect the flux at the inter-microhabitat level (Table 4.12).

Proportional flux from each microhabitat (m^{-2} d^{-1})

	CH_4-C (mg)	CO_2-C (mg)	Total C (mg)	Ratio CH_4-C: CO_2-C	Proportion CH_4-C (%)	Proportion CO_2-C (%)
BB	16.7	235	251.7	1:14.2	6.6	93.4
UH	8.2	390	398.2	1:47.6	2.1	97.9
UL	25.1	80	105.1	1: 3.2	23.9	76.1
UP	17.1	59	76.1	1: 3.5	22.5	77.5
Ratio P:L:H:B	2.1:3.1:1.0:2.0	1:1.4:6.6:4.0	1:1.4:5.2:3.3			

Flux from Burnt Hill blanket bog (m^{-2} d^{-1})

	Area (%)	CH_4-C Absolute (mg)	CH_4-C Propn (mg)	CO_2-C Absolute (mg)	CO_2-C Propn (mg)	Total C (mg)
BB	74.5	16.7	12.44	235	175.08	187.52
UH	1.5	8.2	0.12	390	5.85	5.97
UL	8.0	25.1	2.01	80	6.40	8.41
UP	16.0	17.1	2.74	59	9.44	12.18
Total	100.0		17.31		196.77	214.08

Flux ratios

	Proportional CH_4-C:CO_2-C	Proportion of total, per microhabitat CH_4-C (%)	Proportion of total, per microhabitat CO_2-C	Proportion of total over whole bog CH_4-C (%)	Proportion of total over whole bog CO_2-C
BB	1 : 14.1	6.6	93.4	5.8	81.8
UH	1 : 48.8	2.0	98.0	0.1	2.7
UL	1 : 3.2	23.9	76.1	0.9	3.0
UP	1 : 3.4	22.5	77.5	1.3	4.4
Total				8.1	91.9

	CH_4-C	CO_2-C	Total
P:L:H:B	22.8:16.8:1:103.7	1.6:1.1:1:29.9	2.0:1.4:1:31.4

COOM RIGG

Flux from Coom Rigg bog (m^{-2} d^{-1})
Flux values are taken from Table 4.13.

c) Assume the carbon flux from CR bog is equal to the mean flux calculated from the five study sites, that is, that the study sites are proportionally representing their peat types.

CH_4-C (mg)	CO_2-C (mg)	Total C (mg)	Ratio CH_4-C: CO_2-C	Proportion CH_4-C (%)	Proportion CO_2-C (%)
17.0	278	295	1:16.4	5.8	94.2

d) Calculations repeated as for c), but using only data from sites with similar peat depths as those of MH (i.e. 2-3 m; sites 16 and 17 at CR).

CH_4-C (mg)	CO_2-C (mg)	Total C (mg)	Ratio CH_4-C: CO_2-C	Proportion CH_4-C (%)	Proportion CO_2-C (%)
11.1	485	496	1:43.7	2.2	97.8

e) Calculations repeated as for d), but omitting data from site 17, which may be slightly more minerotrophic, i.e. site 16 only (3.0 m).

CH_4-C (mg)	CO_2-C (mg)	Total C (mg)	Ratio CH_4-C: CO_2-C	Proportion CH_4-C (%)	Proportion CO_2-C (%)
9.7	445	455	1:45.9	2.1	97.9

comparable data from the acid subarctic peatland at Stordalen, Sweden. He calculated total carbon losses of 216 mg m^{-2} d^{-1} C (Svensson 1980), which compares uncommonly well with the lower of the MH figures quoted above. Svensson noted that 11% of this was CH_4-C. At MH the methane proportion was between 8% (present study) and 9% (Clymo & Reddaway 1971).

Methane losses alone accounted for 50-67 mg m^{-2} d^{-1} C at MH and for 10-17 mg m^{-2} d^{-1} C at CR. This may be compared with 24 mg m^{-2} d^{-1} C from the Stordalen mire (Svensson 1980). Harriss *et al* (1985) measured methane flux from a number of Northern Minnesota peatlands (47° 326N, 93° 286W; perched ombrotrophic bogs, mainly *Sphagnum* peat overlying woody, sedge and aquatic plant peat; pH 3.6). Flux ranged between 35 and 146 mg m^{-2} d^{-1} CH_4-C (August, peat temperature 14-20°C at -6 cm). Carbon dioxide emissions were not measured. Methane fluxes previously reported by Harriss, Sebacher & Day (1982), for the Great Dismal Swamp, Virginia (30° 40'N, 76° 30'W) were also low. The swamp is a forested peat bog, and in the 17 months between September 1979 and February 1981, CH_4-C flux ranged between less than 0.75 and 15 mg m^{-2} d^{-1} C. Carbon dioxide flux was not measured. During the Antarctic summer (December to March) 1981-82, Yarrington & Wynn-Williams (1985) measured methanogenesis from a waterlogged (soligenous) moss peat where the mean summer temperature at -1.5 cm was 2.1°C. Fluxes measured *in situ* ranged between 0.02 and 15.2 mg m^{-2} d^{-1} C. The peat was, on average, only 13 cm deep.

Other studies of methane flux have been made (e.g. Williams 1980; Williams & Crawford 1984; Goodwin & Zeikus 1987), but cannot be compared because of non-standardised methodologies. However, it seems clear from the results quoted above that both absolute and proportional methane emissions from MH at least, compare well with those of the Stordalen subarctic acid peatland, but that methane emissions from other wetland types differ considerably. Compared with the present results, methane losses from the other wetlands span a wide range, extending two orders of magnitude below the lowest recorded here and one order of magnitude above. Maritime tundra-like sites appear to be intermediate between the maritime Antarctic and temperate peat wetlands, in terms of their CH_4-C losses. Whatever the

exact figure, it is clear that the reults from any given area cannot be used as a basis for calculating carbon losses from other wetlands, and as yet we are far from being able to make confident, accurate, predictions for other, less accessible, wetland regions. This is particularly pertinent when the current interest and concern over climate change is considered.

6.7 GLOBAL CARBON CYCLING AND ATMOSPHERIC CHEMISTRY STUDIES

It is now clear that both methane and carbon dioxide may be of importance in thier contribution to the perceived problem of global warming because of their capacity to absorb infrared radiation. The atmospheric concentration of CO_2 is approximately 380 ppm and of CH_4 about 1 ppm. CH_4 has about a 30-fold higher absorption capacity than CO_2, but CO_2 is absolutely more important because of its higher concentration. Counter to this is the fact that CH_4 is a reactive gas in the atmosphere, whereas CO_2 is much less so. It has therefore become of great interest to know what are the main sources of the gases, where these are located, and their respective contributions. Carbon dioxide concentrations in the atmosphere have long been studied in other contexts, but information about methane has only started to be gathered relatively recently. It is widely believed now that the atmospheric concentration of methane is increasing at a significant rate (Ehhalt 1974, 1985; Graedel & McRae 1980; Craig & Chou 1982; Rasmussen & Khalil 1986). The figure of 1-2% increase per annum for the troposphere (the lowest 10 km of the atmosphere) is frequently quoted. A number of independent studies have led to the conslusion that about 90% of atmospheric methane is from biogenic, rather than anthropogenic, sources (e.g. Ehhalt & Schmidt 1978; Sheppard *et al* 1982). Furthermore, a significant discrepancy has been discovered between atmospheric methane concentrations in the northern (higher) and southern hemispheres (Rasmussen & Khalil 1986), and again between high and medium latitudes compared with the equator (Ehhalt 1985, and see Oberbauer, Oechel & Riechers 1986).

It follows that the vast areas of northern peatlands lying between about 45° and 65°N (see Chapter 1) are likely to represent an

important source of global atmospheric methane. Despite this, morthern peatlands have been much neglected, and estimates of tundra and taiga methane emissions have been made by extrapolation and adjustment of emission rates from other systems. However, even a cursory glance at the differences in the component fluxes from the different microhabitats in Table 6.1 will serve to illustrate how inaccurate this is likely to be. At MH, about 50x more carbon was lost as carbon dioxide than as methane from hummocks, and almost exactly the same ratio was reported from Burnt Hill by Clymo & Reddaway (1971). From the wetter lawn and pool areas the ratio was reduced to about 3x, reflecting the relatively high methane fluxes from these areas. In comparison, at Stordalen, Svensson (1983, Introduction) reported a maximum of only 0.1% of the total carbon flux as methane from dry ombrotrophic areas, and 5.5% from the wet ombrotrophic areas. The trends are similar, but not the proportions. Thus, as has been noted form various results of the present study, the gross water level (and probably also the water *content*) has an effect on the relative and absolute methane and carbon dioxide fluxes. The vast extent of true northern tundra (occupying almost 5.5 million km^2; Danks 1981) is underlain either by continuous or discontinuous permafrost, accounting for 26% of the earth's land surface (Sage 1986). The top of the permafrost undergoes annual freeze-thaw cycles. Stordalen and the Antarctic site (Signy Island) used for the methane studies quoted above also experience such cycles. Consequently, the water levels and the water content of the peat there change throughout the year (as indeed they do also in non-permafrost areas, including MH and CR). The effect on (the annual) methane and carbon dioxide emissions of such a cycle is not known. It was once commonly stated that there was no microbial activity below 0°C, but this has since been shown not to be the case (Heal, Latter & Howson 1978; Flanagan & Bunnell 1980; Wynn-Williams 1980; Clymo 1983). Methane and carbon dioxide emissions were very low at times during the present study when the ground surface was frozen, and when patchy snow was lying, but were not zero, and in any case would not necessarily reflect no *production*. Hence, any measurements made during the summer months on tundra areas subject to permafrost, will probably bear little relation

to the situation in autumn and winter. At the highest latitude, the 'summer' (growing season) lasts for only about six weeks. For the remainder of the year the permafrost is closer to the surface. We need much more information about methane and carbon dioxide fluxes over the different tundra microhabitats, over the annual permafrost cycle, before we can begin to approach any sort of realistic estimate of the contribution of these areas to global carbon cycling, and hence, perhaps, global warming.

In addition to the question of large-scale changes in microhabitat on an annual cycle, there is one of the effect of mineral additions. Inundation of land during a spring thaw redistributes solutes, and many areas with extensive peatlands experience windblown mineral deposits originating, for example, from volcanic ash outfalls or fine glacial loess. It has already been noted that minerotrophic areas tend towards higher methane losses, and this is also indicated by the CR values in Table 6.1 (compare d) and a) values). Again, it is not known what effect such inputs would have, considered on the larger scale at which they might apply in regions such as Iceland and Greenland, and indeed on peatlands fringing permanent ice margins where glacial sandur valleys are extensive.

6.8 SUMMARY

The results of the present study represent a relatively detailed monitoring programme of the gaseous carbon content and flux of two temperate ombrotrophic peatlands. In the previous (Quantitative) Discussion chapter they were used to validate certain assumptions on which a current model of peat decay and accumulation is based (Clymo 1984).

The second chapter of the Discussion has considered the factors affecting gaseous carbon production and loss from blanket peat, based mainly on the results of monitoring chemical characteristics of the profiles concerned. Results agreed generally with the findings from previous work, particularly in the importance of waterlogging / redox potential and temperature. From rather patchy data it has been possible to arrive at new ideas which can now be investigated further

to help clarify the very complex interrelations between these and other factors involved.

Finally, brief attention has been given to the relevance of this study with respect to current interest in the process of climate change. Methanogenic peatland areas are most extensive at high northern latitudes, where the nature of the habitat varies considerably both spatially and temporally. Many more basic data are needed before we can begin to estimate this contribution to the increase in global atmospheric methane and carbon dioxide, and much must be learned of the mechanisms involved if we are to move towards making confident, accurate predictions about carbon losses.

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APPENDICES

APPENDIX A. DOMINANT PLANT SPECIES AT FIELD SAMPLING SITES

	Microhabitat	Vascular spp.	*Sphagnum* spp.
a) Moor House			
Site 4	Lawn	*Eriophorum angustifolium* *Drosera rotundifolia*	*S. papillosum*
Site 5	Pool	*Eriophorum angustifolium*	*S. cuspidatum*
Site 6	Hummock	*Calluna vulgaris* *Erica tetralix* *Eriophorum angustifolium* *Scirpus caespitosus* *Narthecium ossifragum*	*?S. palustre* *S. capillifolium*
Site 7	Lawn	*Drosera rotundifolia* *Eriophorum angustifolium*	*S. papillosum* *S. cuspidatum*
Site 8	Pool	*Eriophorum angustifolium*	*S. cuspidatum*
Site 9	Hummock	*Calluna vulgaris* *Erica tetralix* *Scirpus caespitosus* *Eriophorum angustifolium* *Narthecium ossifragum*	*S. papillosum* *S. imbricatum*
Site 10	Lawn	*Eriophorum angustifolium* *Narthecium ossifragum*	*S. papillosum* *S. cuspidatum* *S. imbricatum*
Site 11	Pool	*Eriophorum angustifolium*	*S. cuspidatum*
Site 12	Hummock	*Vaccinium oxycoccos* *Rubus chamaemorus* *Empetrum nigrum* *Eriophorum angustifolium*	*S. papillosum* *S. magellanicum*
b) Coom Rigg			
Site 13		*Scirpus caespitosus* *Eriophorum angustifolium* *Erica tetralix* *Narthecium ossifragum* *Andromeda polifolia*	
Site 14		*Eriophorum angustifolium* *Scirpus caespitosus* *Erica tetralix* *Drosera rotundifolia* *Narthecium ossifragum* *Andromeda polifolia* *Vaccinium oxycoccos*	*S. magellanicum* *S. capillifolium* *S. cuspidatum*
Site 15		*Eriophorum angustifolium* *Scirpus caespitosus* *Erica tetralix* *Narthecium ossifragum* *Vaccinium oxycoccos*	*S. imbricatum*

APPENDIX A

	Vascular spp.	*Sphagnum* spp.
Site 16	*Calluna vulgaris* *Eriophorum angustifolium* *Erica tetralix* *Narthecium ossifragum* *Scirpus caespitosus* *Drosera rotundifolia* *Vaccinium oxycoccos*	*S. magellanicum*
Site 17	*Eriophorum angustifolium* *Narthecium ossifragum* *Scirpus caespitosus* *Festuca rubra* *Molinia caerulea*	*S. recurvum* *(Polytrichum commune)*

APPENDIX B. SPECIFICATIONS OF GAS SAMPLER PARTS

Rubber inner	Thickness 0.05 mm, overall length 17.5 cm, diameter 3.3 cm. LRC Products Ltd., London.
Expanded aluminium outer	Length 20.5 cm, diameter 3.5 cm.
Rubber bung (ends)	Size 35 (upper diameter 4.0 cm, lower diameter 3.5 cm), cut into two: top section 1.25 cm high, bottom section 2.5 cm high.
Brass U-tube	Length 9.3 cm, I.D. 1.77 mm, O.D. ≈3.5 mm.
PVC tubing	I.D. 2.0 mm, O.D. 4.0 mm.
3-way nylon tap	(Medical) The Genito Urinary Manufacturing Company Ltd., London W1N, or Southern Syringe Service Ltd., London N14.

APPENDIX C. TESTS OF GAS SAMPLER PROPERTIES

A number of trials were carried out in the laboratory and the field to test the proposed design of the gas samplers.

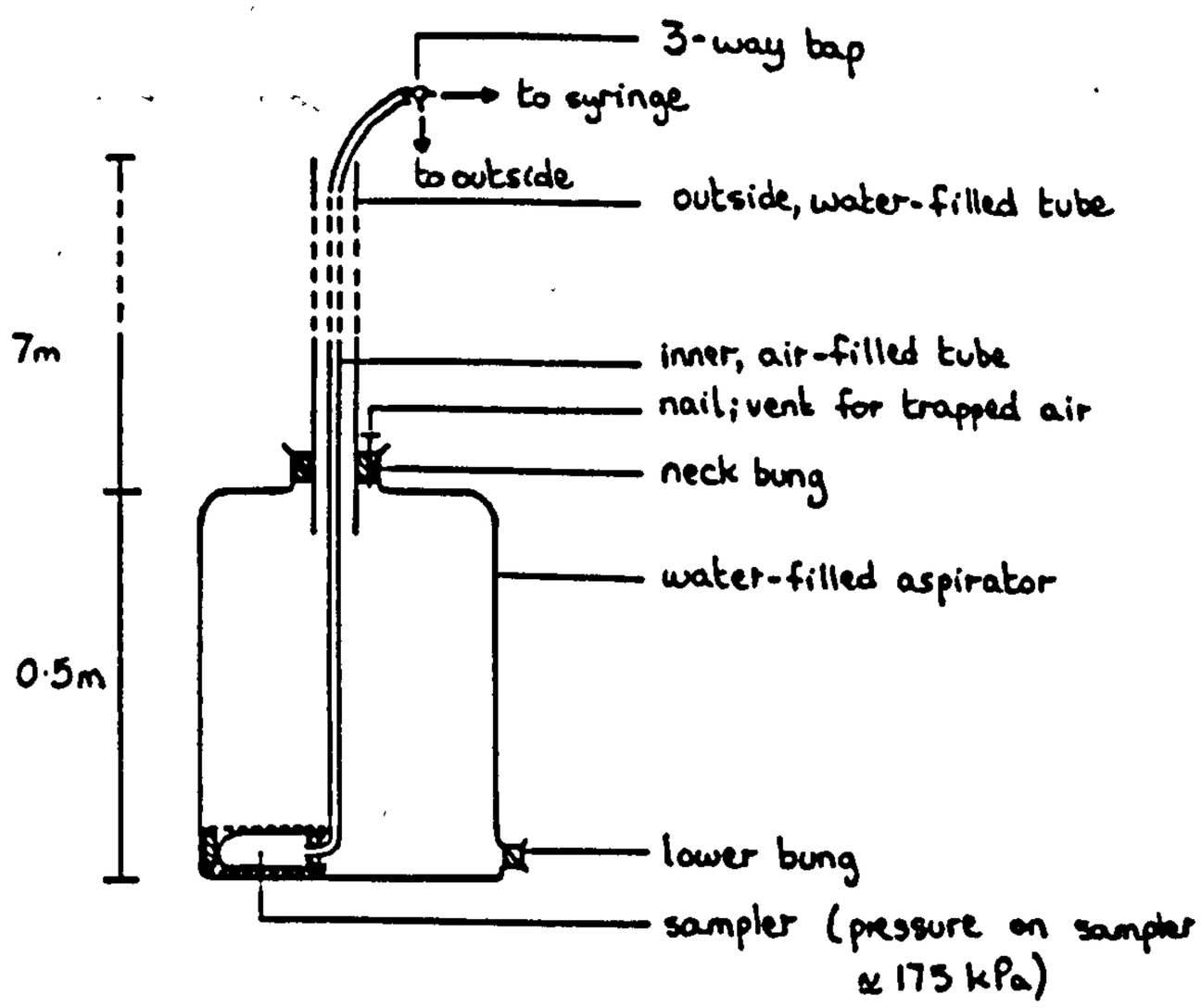
a) Integrity against leaks

First it was established that the inners could be made gas-tight (against mass flow) and water-tight by assembling a sampler, inflating it and then immersing it in water. No gas bubbles were evolved from it, and on retrieval after 15 minutes no water was found to have leaked into the inner.

b) Properties under pressure

Samplers buried in the peat will have additional pressure acting on them. It was reported (Chapman 1964a) that one of the field sites to be used had peat deposits of up to 8 m in some areas, so samplers were tested under pressures approximating to those at that depth. The apparatus to develop the necessary pressure is illustrated in Fig. C.1, in which an assembled sampler is shown in a water-filled, sealed aspirator and a 7 m water-filled pipe leads vertically from the aspirator to develop the extra 75 kPa pressure simulating conditions

FIG. C.1 Apparatus to test gas sampler under pressure



7.5 m down in the peat (see Section 3.1.1, Properties of Samplers). The sampler was connected to the 'surface' by an air-filled pipe within the wider water-filled one. By filling and deflating the sampler from 7 m above the aspirator, and by leaving the air-filled sampler in position for three weeks, the properties of the sampler were tested. At the end of the experiment the sampler was deflated, but had no water inside it. Thus it was established that a sampler under approximately 175 kPa pressure could be inflated and deflated repeatedly, was permeable to air in at least one direction (outwards) at a sufficiently rapid rate to be considered reasonable for gas sample collection in the field, assuming that the diffusion rates of CH_4 and CO_2 are not very different from that of air, and that the sampler would remain water-tight, at least over a period of three weeks.

c) Gas sampler trials in peat

An assembled sampler was positioned at the bottom of minibog M2 using a peat-boring extension rod to force it down a pre-bored hole. Immediately this was done, the wet peat moved in from the sides to back-fill the hole above the sampler. The sampler was successfully inflated from the surface, and after three days in the minibog a gas sample was withdrawn without difficulty into a 60 cm^3 plastic syringe.

Following these successful trials, samplers of the proposed design were installed in the field and were found to be fully functional.

d) Effect of peat on gas sampler inners

In February 1982 an assembled gas sampler was buried in a minibog in the experimental garden at Westfield College and was left in position until April 1984, when it was retrieved and inspected for damage. There was no visible change in the rubber, and the inner did not tear when pulled. It held air without leaking, even under pressure.

e) Surface gas sampler equilibration time

An experiment to determine the rate at which an equilibrium is established between the concentration of gases on both sides of the surface sampler membrane was twice set up in the experimental peat plot. An inflated sampler was put on each of a group of peat cores, representing each of the three microhabitats to be found in the field (viz. pool, lawn, hummock). The buckets containing the peat cores were covered for the duration of the experiment, and samples of gas from inside the samplers and from the atmosphere inside the bucket around them were taken at regular intervals over a period of three days. After each sample, an equal volume was replaced with N_2.

The value of the results from the first run of this experiment is very limited, since the covers on the buckets were unsatisfactorily sealed, so that peat gas could escape, erratically. However, the results suggested that the flux of methane was greater from the pool peat surface than from the hummocks, whereas the converse was true for carbon dioxide; that the concentration range of the gases to be measured was large; and that the equilibration time was likely to be a matter of days, rather than hours.

The results from a repeat experiment in which more peat cores were used and the bucket lids were sealed on indicated that the surface flux of methane and carbon dioxide was linear over a period of two days, for each peat type. The correlation coefficient, r, ranged from 0.92-1.00 for the linear regression of the mean (n = 3) CH_4 concentration in the bucket against time, and from 0.93-0.98 for that of CO_2 (means of 3). After two days, the mean (n = 3) proportion of the surrounding bucket atmosphere concentrations measured in the samplers was 67%, 66% and 73% for CH_4, and 98%, 98% and 96% for CO_2 over hummocks, lawns and pools respectively. At the time of this repeat experiment a sampling period for surface gas samplers of 2 days had already been implemented and it was decided to continue with this throughout, because with a linear surface flux over this period the sampler-atmosphere concentration discrepancy, and hence the surface flux, could be estimated.

An experiment was carried out concerning the rate of movement of gases through the sampler membrane in order to determine whether CH_4

and CO_2 diffused through at equal rates in both directions. This was done by placing a pair of samplers inside the same bucket, one of which was assembled with the inner turned inside-out. The bucket lids were sealed on and samples from the bucket atmosphere and from both samplers were taken at intervals over a 48h period. Duplicate pool and hummock buckets were used. A paired t-test was carried out separately for the results from each bucket for CH_4 and CO_2, between the concentrations measured in the 'normal' sampler and those in the 'reversed' sampler. In two out of the eight tests there was no significant difference between the concentration of gas measured in the two samplers, but in four cases the null hypothesis was rejected at the 5% level and in two cases at the 1% level of significance. Overall, it appeared that there was a difference in the diffusion behaviour of the gases through the 'normal' and 'reversed' membranes. In all cases where a difference occurred, the 'reversed' membrane showed a higher concentration of both CH_4 and CO_2 initially, compared with the 'normal' inner. Over the pool peat this discrepancy gradually decreased with time, as it did over the hummock peat, but here the decline was more erratic. A paired t-test between the concentrations in the 'normal' and 'reversed' samplers at 48.0 hours only showed no significant difference between them. In practice, surface gas samples were always taken at the end of a two-day sampling period, both in the experimental peat plot and in the field. Any difference in the rates of diffusion of CH_4 and CO_2 in and out of the sampler in the period up to 48 hours will effectively be zero by the time the sample is withdrawn. In any event, the effect of such an imbalance between the rate of diffusion in and out of a sampler will only serve to increase the time necessary for an equilibrium to be established between the contents of the sampler and its surroundings; it will not alter the usefulness of the sample collected. Further, the samplers used for regular monitoring of surface gas flux (and deep peat gas concentrations) were always assembled with the inner the same way out, thus eliminating any possible errors due to such inconsistencies of diffusion rate as are suggested by the results of the 'reversed' sampler experiment.

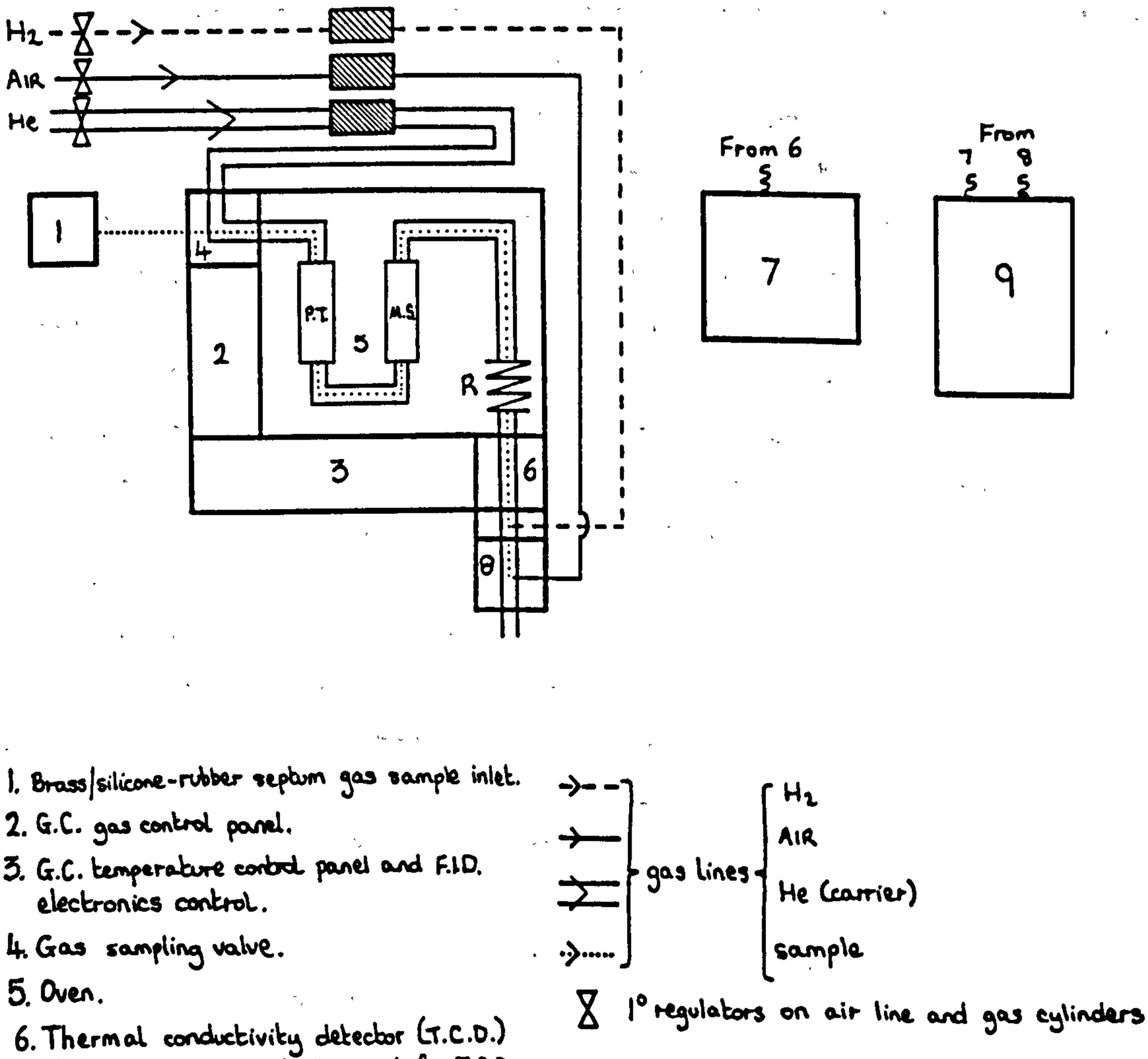
APPENDIX D. ANALYSIS OF GAS SAMPLES

Gas samples were analysed using a Perkin Elmer Sigma 3B gas chromatograph (GC), the output was in graphic form via a Linseis (model LS44) chart recorder. The resulting peaks were quantified manually, using peak height.

a) Gas chromatograph configuration

The GC apparatus is represented schematically in Fig. D.1. The Sigma 3B is equipped with two channels. Only one of these

FIG. D.1 GC apparatus for the analysis of gas samples

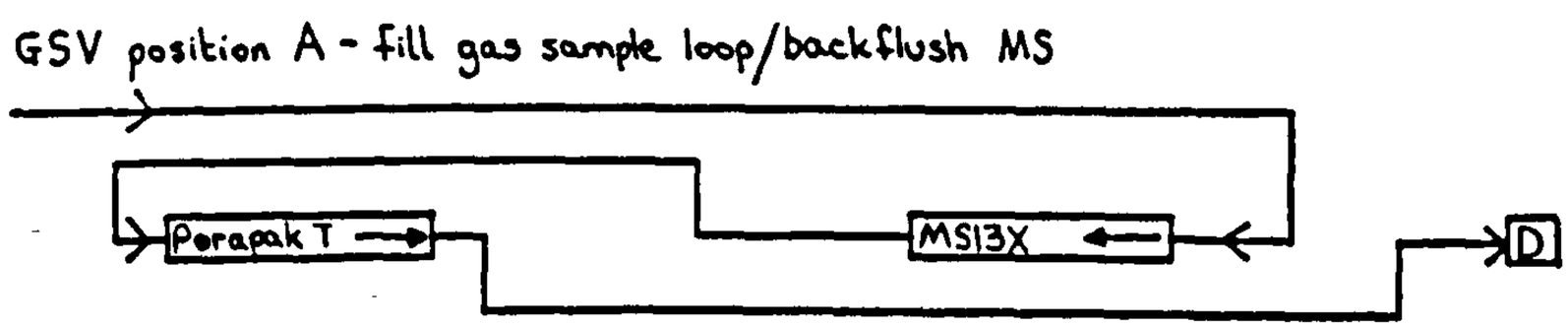


was used for the gas analyses. A dual column system was installed, consisting of a 4 m column packed with the porous polymer Porapak T, followed by a 1 m column in series, packed with molecular sieve MS13X. No liquid phase was present. Both columns were ⅛" stainless steel, and in each case the packing mesh size was 80-100. Two columns were necessary because of the need to separate the oxygen and nitrogen fractions of air, and a number of lighter hydrocarbons. Molecular sieve will separate O_2 and N_2, but tends to retain the hydrocarbons beyond a reasonable analysis period. Porous polymers separate most gases (but not air components), including the lighter hydrocarbons, efficiently. MS13X was used because retention times are shorter than for MS5A while separation is still complete. Porapak T was used because it is polar, and such porous polymers separate the lighter hydrocarbons easily and consistently. Furthermore, being polar, it retained any carbon dioxide longer than a non-polar polymer could have done (for a given length of column), thereby allowing the air components in a sample the time to pass through the molecular sieve before eluting from the Porapak column, and thus delayed the time at which it could have entered the molecular sieve. This was a significant feature because the main disadvantage with molecular sieve is that it strongly retains CO_2; if carbon dioxide enters a molecular sieve column it may be held up for a matter of hours and cause interference with later samples. By calculating relative retention times for the various components in different lengths of column it was possible to decide on a combination which allowed for the complete passage through both Porapak and MS columns of O_2 and N_2 (and CH_4) before the CO_2 had begun to elute from the Porapak. At this stage (i.e. after the elution of CH_4) the order of the columns was reversed and at the same time the MS column was backflushed. By doing so, the CO_2 was prevented from entering the MS because after switching this became the second column in the system and components eluting from it passed immediately to the detectors. The separation of the hydrocarbons above methane was able to continue in the Porapak and these components, similarly, were detected as they eluted from the column. The column configuration is illustrated in Fig. D.2.

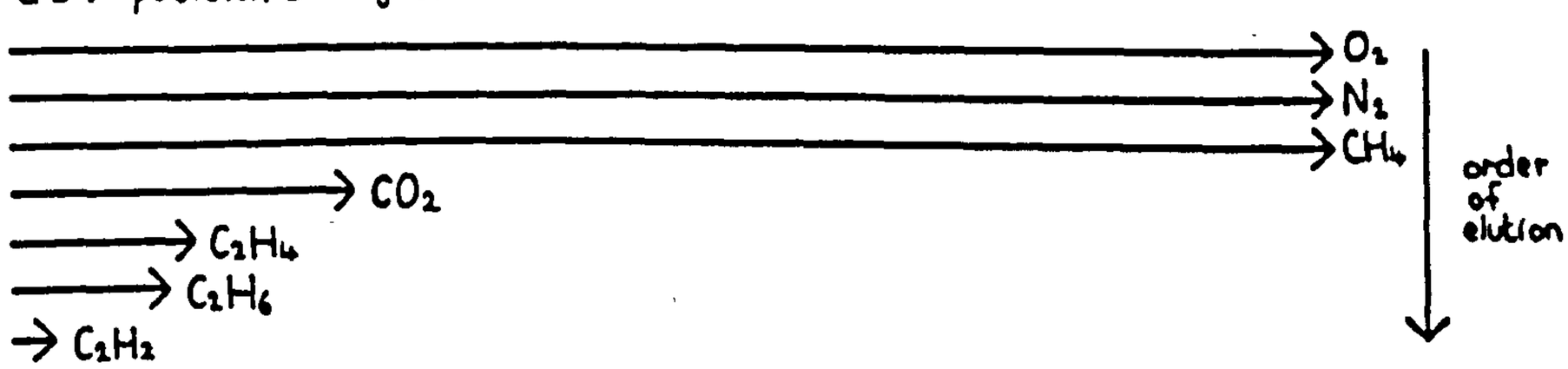
APPENDIX D

FIG. D.2 GC column arrangement

a) Order and direction in which carrier gas flows through columns.



b) Diagrammatic representation of component movements in column system during the analysis of a peat gas sample. (Compare with a), above.)

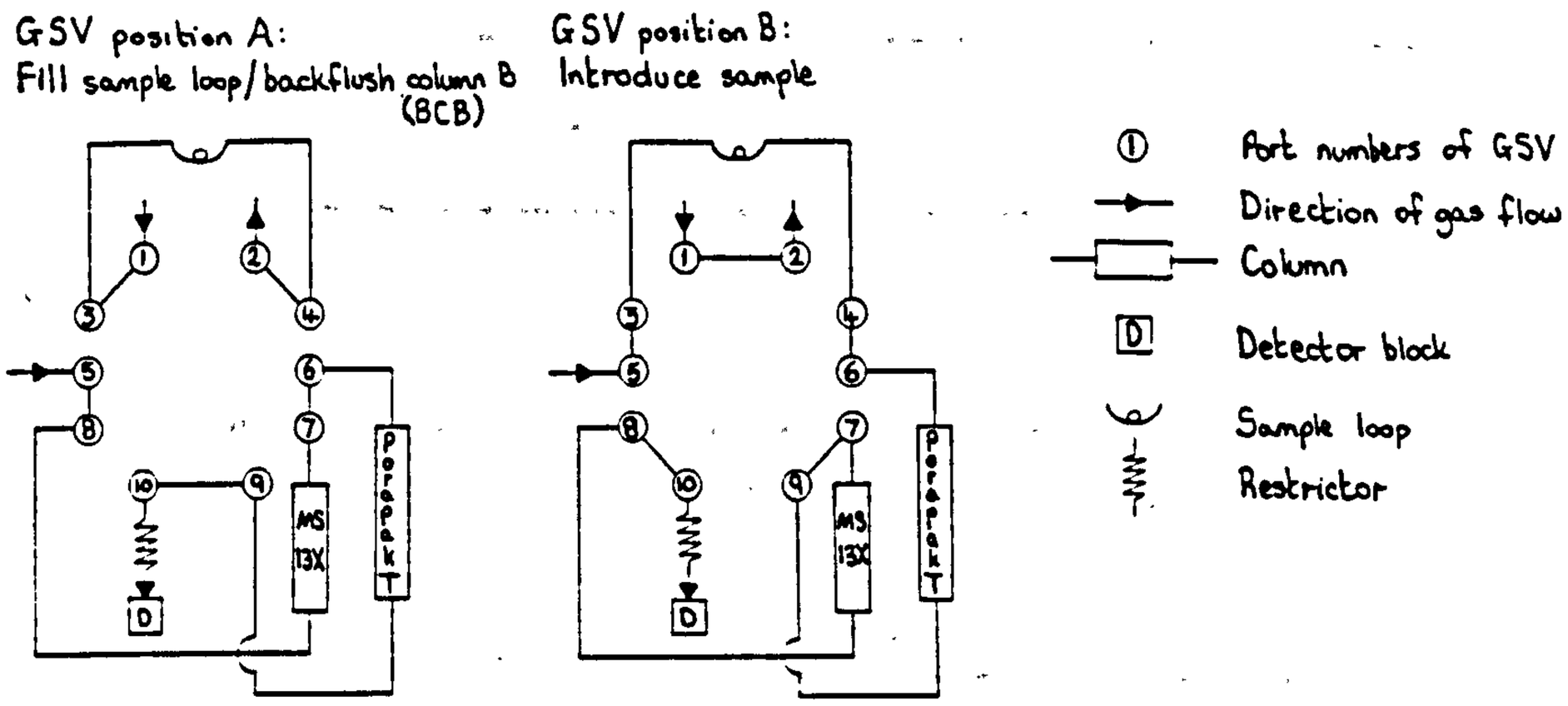


Operation of this system was effected through a 10-port gas sampling valve (GSV). In position B (Fig. D.3) the sample loop is connected in, and the sample is flushed out by the carrier gas and forwards into the Porapak column, then through the MS and finally into the detector block. In position A the sample loop is filled, while it is disconnected from the columns. Carrier gas flows first through the MS, backflushing it, and secondly through the Porapak ('forwards') before eluting through the detectors.

FIG. D.3 Operation of gas sampling valve

In position A, the sample loop is filled, while it is disconnected from the columns. Carrier gas flows first through the MS, backflushing it, and secondly through the Porapak ('forwards') before eluting through the detectors. In position B the sample loop is connected in, and the sample is flushed out by the carrier gas and forwards into the Porapak column, then through the MS and finally into the detector block.

Order in which the carrier gas flows through the valve ports:
Position A: 1-3-L-4-2 / 5-8-M-7-6-P-9-10-R → D
Position B: 1-2 / 5-3-L-4-6-P-9-7-M-8-10-R → D



A restrictor was positioned immediately before the detector block to prevent a direct surge of pressure acting on the flame ionisation detector (FID) and thermal conductivity detector (TCD) when the GSV was operated. Furthermore, the TCD response is dependent on carrier gas flow rate, and so ideally this should be kept constant. In practice this is not possible to achieve and although the restrictor improves the stability of the flow rate at the time of switching, there follows a period in which the TCD gradually resumes its original steady baseline. The response of the FID is independent of carrier gas flow rate, but a sudden change can extinguish the flame and so the FID needs protection from the switching pressure surge.

Components eluted from the final column passed through the detector block housing a TCD and a FID in series. The TCD responded to all the components, but was only sufficiently responsive to O_2, N_2 and CO_2 to allow quantification of the peaks. The hydrocarbon components were detected as they passed through the FID. On the most

sensitive settings the TCD and FID could be used to detect component concentrations of less than 1 vpm. This is equivalent to approximately 7 x 10^{-4} ppm CH_4 or 2 x 10^{-3} ppm CO_2. The operating principles of the TCD and FID are described by McNair & Bonelli (1969).

b) Gases for GC operation

The carrier gas used was helium. Its thermal conductivity is high compared to that of the components to be measured, resulting in a larger drop in temperature as a component passes over the filament of the TCD and thus an increase in the detector response. In addition, because helium is non-flammable, it serves to maximise the response from the FID. Although N_2 is often used as a carrier, and has the advantage over helium of being much cheaper, it could not be used here because of the wish to detect N_2, and O_2 (to act as a check on air contamination of samples and to measure the relative concentration of O_2 and CO_2). The optimal carrier gas flow rate, at which the column system is acting most efficiently, was determined experimentally. Samples of air were run through the GC and the carrier gas flow rate was increased by 5 cm^3 min^{-1} for each successive analysis. Using the CH_4 peaks, the highest equivalent to a theoretical plate (HETP), a measure of the efficiency of a column system, was evaluated (McNair & Bonelli 1969). Optimal carrier gas flow was determined to be 29.5 cm^3 min^{-1} He; in practice it was set to 30 cm^3 min^{-1}.

The FID requires a supply of H_2 and air (O_2). A flow of hydrogen is introduced into the gas eluting from the TCD and then the mixture is burned in air. Although the response of the FID is not directly dependent on carrier gas flow rate, its performance is dependent on a number of other factors including the correct choice of all flow rates. The supply of air to the FID was at the pressure suggested in the Sigma 3B manual (207 kPa), as was that of H_2, although the H_2 setting was later increased (to 138 kPa) to facilitate ignition, without significantly affecting the response.

Gases were passed through a drying agent (molecular sieve) between the primary regulators on the cylinder or air line, and the secondary regulators on the GC gas control panel, to remove water and

prevent it deactivating the MS column. The drying agent was reconditioned each time a new gas cylinder was used.

c) GC operating conditions

It is evident from the foregoing sections on GC configuration and gases that there are a large number of factors and conditions which interact to produce the final GC performance; in some cases ideal conditions may have to be compromised in order to optimise two or more conflicting requirements. Any one factor, if changed, may alter the performance of the GC so it is essential to report the conditions under which any result is obtained, and if results are to be easily compared, the conditions should remain constant for all the analyses. Bearing in mind the large number of samples to be analysed, and the range of components and concentrations that early samples had contained, an initial period was taken to establish the optimum conditions for the present purpose, and then all the gas samples were analysed according to the following instrument conditions:

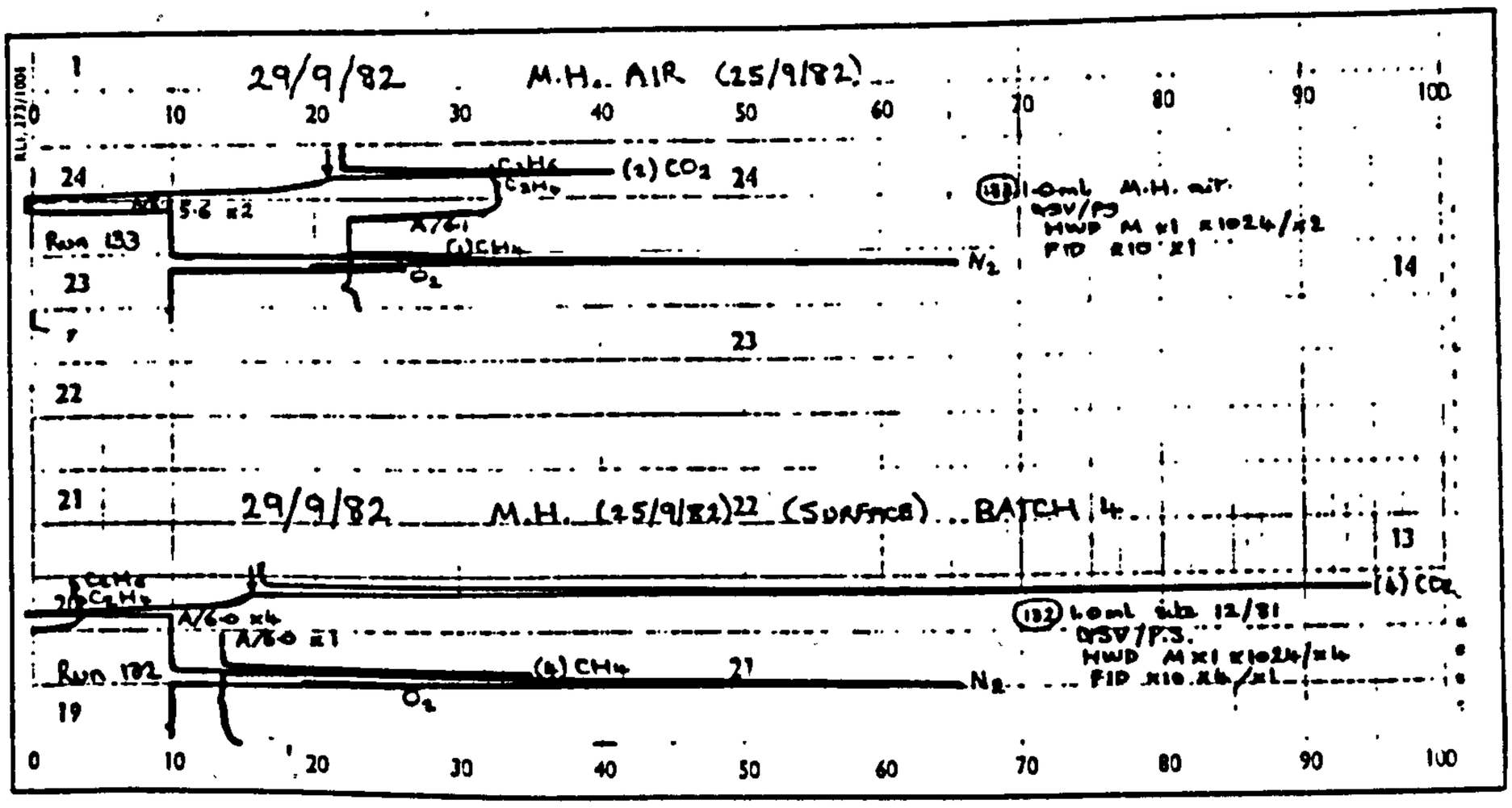
Carrier gas, He, inlet pressure at 1° regulator
517 kPa (75 psi), flow rate 30 cm^3 min^{-1}
Air pressure 207 kPa (30 psi)
H_2 pressure 138 kPa (20 psi)
Sample volume 1.0 cm^3
Injector block temperature 75°C
Oven temperature 50°C
Detector block temperature 75°C
TCD filament current medium (240 mA)
(Chart speed 200 mm h^{-1})

The range and attenuation settings of the relevant detector for each component peak were written on the chart as a sample was analysed, for reference later in quantification. The GSV was actuacted, to switch the columns, 6.0 minutes after a sample was switched in. Under these conditions, typical retention times since sample introduction, were as follows (minutes):

O_2 2.4; N_2 2.6; CH_4 4.2; CO_2 7.5; C_2H_4 8.0; C_2H_6 8.7; C_2H_2 16.9.

APPENDIX D

FIG. D.4 Sample chromatogram



A sample was usually run for only 9-10 minutes once it had been established that there was no significant concentration of ethyne (C_2H_2) present. A sample chromatogram is reproduced in Fig. D.4.

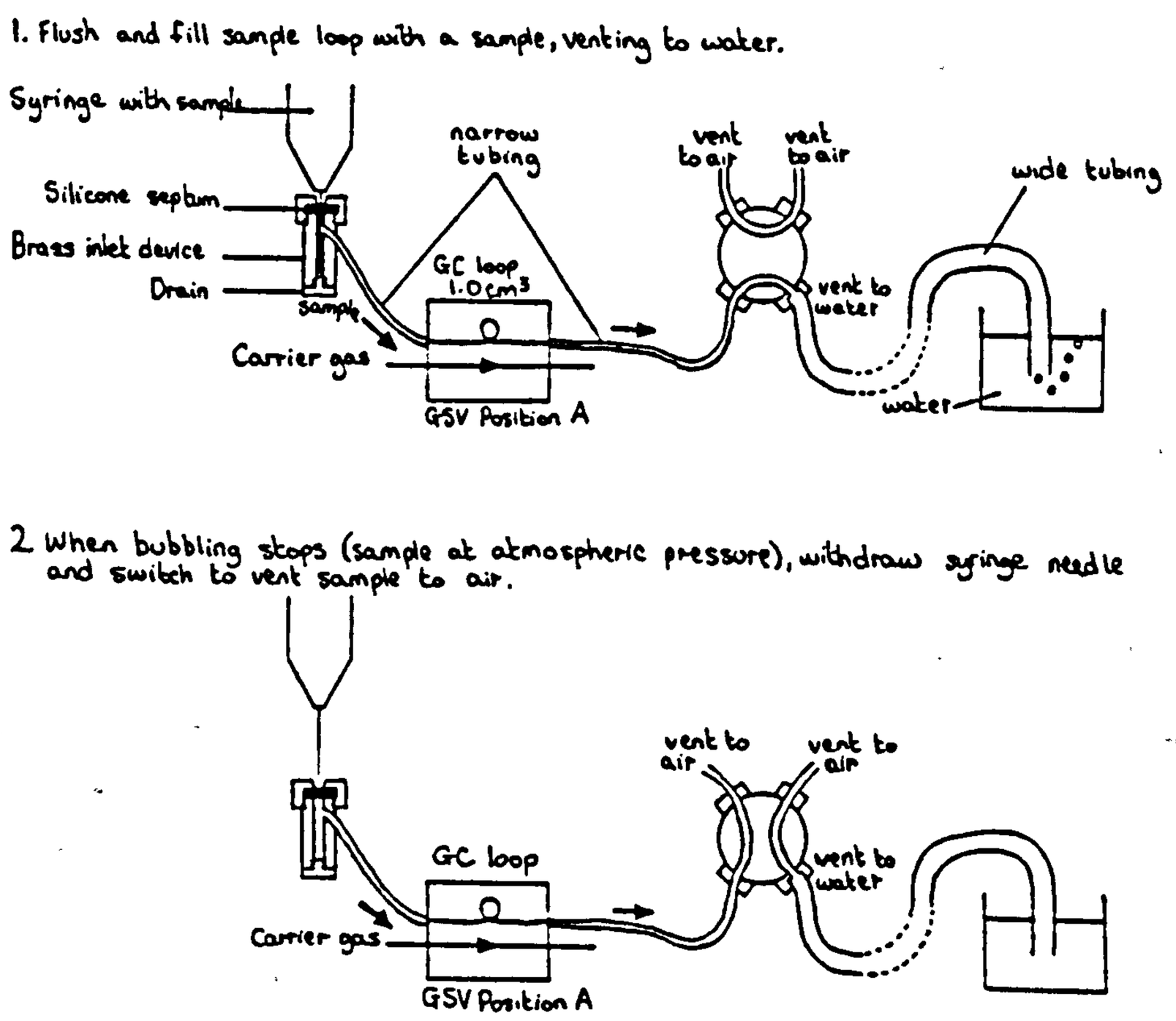
d) Injection of gas sample

Sample injection is a technique which must be standardised if recorder peaks are to be comparable. A sample must be injected quickly, but smoothly, to avoid pressure surges with the resultant effect on peak shape. A sample should be injected as a single 'plug' of gas to avoid trailing peaks. This is particularly important when peak height is to be used for quantification, rather than the accurate measure of peak area, because the difference between the peak height and its area will increase with increasing length of peak baseline. The exact volume of the sample must be known, and should be constant, in order to calculate the total mass of each component. Furthermore, the sample must be injected at a known, constant pressure to prevent concentration inconsistencies within the sample volume and changes in gas flow rate, both of which would result in inaccuracies during quantification.

APPENDIX D

Constant sample volume was achieved through the sample loop of the GSV, which held exactly 1.0 cm^3 of sample and switched this instantaneously into the carrier gas flow. With the GSV in position A the loop was disconnected from the column system and was open at both ends to the atmosphere, via two lengths of capillary tubing (Fig D.5(1)). The inlet side of the tubing was fitted with a brass device to hold a silicone rubber septum through which the sample was injected.

FIG. D.5 Method used to introduce 1.0 cm^3 of gas sample, at atmospheric pressure, onto the GC column



The brass holder was solid except for a hole bored down the centre of its long axis to take the syringe needle so that the sample was injected at the head of the capillary tubing leading from its bottom end. The dead volume around the needle was negligible (0.018 cm^3). The septum was fitted snugly over the top end of the brass device and was held in place by a brass cap which screwed down onto it, and allowed it to be changed easily. The outlet tube from the sample loop vented through a water-filled beaker (volume 15 cm^3). A sample was injected through the septum and flushed the loop clean of the previous sample; it vented via the water. After flushing the loop with several cm^3 of sample the syringe was sealed (3-way tap), the needle withdrawn from the septum and when the bubbles from the outlet tube stopped, the GSV was actuated, thus introducing the contents of the sample loop - 1.0 cm^3 of sample at atmospheric pressure - into the carrier gas flow (Fig. D.5(3)). Once the contents of the loop were seen to be at atmospheric pressure, and before the syringe was removed or the GSV actuated, another device was used to switch the loop outlet tube to vent to air, rather than through the water (Fig. D.5(2)). This, in addition to the long length of slightly under-diameter outlet tubing, ensured that any pressure changes occurring when the loop was switched in, did not result in water being drawn into the GSV tubing, in the unlikely situation that the pressure in the column was lower than atmospheric. As a further safeguard, the loop was left to vent to air whenever the GC was not in use.

e) Quantification of chromatogram peaks

The area under a peak is proportional to the total mass of eluted component, and when the volume is constant, it is proportional to the concentration. Measuring the area accurately by hand is difficult and time-consuming. As a compromise, peak height is often used, and this method was adopted here. The very narrow, symmetrical peaks and the steady baseline for all components (except CO_2) made measurement unambiguous. The CO_2 peak was not symmetrical and, which was more of a problem, its baseline was not level and did not show a consistent slope from sample to sample. The deviation from a steady baseline was due to the slow recovery of the TCD after GSV switching. This can be seen in Fig. D.4, above. The only constant feature of the CO_2 peak

was a 'shelf' towards the base of the leading edge, marked with an arrow in Fig. D.4, so the CO_2 peak height was measured as the vertical distance between this and the top of the peak. It is suspected that this has led to underestimates of CO_2 in some cases.

A direct calibration of the GC was carried out for all components as a first priority on each analysis day. Occasionally, calibrations were carried out at intervals throughout the day to determine the extent of any drift, and this was found to be negligible; indeed, there was no significant change in the calibration over the whole three-year period that the GC was in use. To calibrate the machine 1.0 cm^3 of a standard calibration gas mixture (Phase Separation, Clwyd) was run under the normal GC conditions detailed in c), above, and the peak heights measured in chart divisions. The composition of the standard mixture was given as the concentration of each component, in vpm (this can be converted to percentage concentration (v/v) by multiplying by a factor of 1×10^{-4}), so all calibration values and quantification of sample peaks were calculated in vpm units and converted to ppm (w/v) or total mass as necessary. The final results are quoted in ppm ($\equiv \mu g\ cm^{-3}$), Table D.1.

TABLE D.1 Factors used to convert component concentration in vpm (v/v) into ppm (w/v).

O_2	1 vpm $\equiv 1.43 \times 10^{-3}$ ppm
N_2	1 vpm $\equiv 1.25 \times 10^{-3}$ ppm
CH_4	1 vpm $\equiv 7.14 \times 10^{-4}$ ppm
CO_2	1 vpm $\equiv 1.96 \times 10^{-3}$ ppm

Having obtained the conversion factors, per chart division, for each component at the range and attenuation settings on the TCD and FID always used for the calibration (here referred to as the primary conversion factors, 1° CF), these were themselves 'standardised' to give the corresponding conversion factors at the most sensitive range and attenuation settings likely to be used, or, in the case of O_2 and N_2, at the TCD settings at which they were always analysed because of their high concentration. These are referred to as the secondary conversion factors (2° CF) and they facilitated the quantification of

large numbers of peaks traced at a range of sensitivities. Table D.2 gives an example of this.

TABLE D.2 Derivation of a typical set of primary and secondary conversion factors from a calibration trace, for the quantification of unknown sample peaks.

Component	Concentration in standard gas mixture (vpm)	Detector	Calibration 1° C.F. settings		Calculation 1° C.F. (vpm per chart division)	Calculation 2° C.F. settings for 2° C.F.		Calculation 2° C.F. (vpm per chart division)
			Range	Att^n		Range	Att^n	
O_2	150000	TCD	x1	x1024	12600	x1	x1024	12600
N_2	984551	TCD	x1	x1024	17000	x1	x1024	17000
CH_4	1100	FID	x100	x4	23,3	x10	x1	0,6
CO_2	5200	TCD	x1	x8	116,9	x1	x1	15

Results of experiments in which different GC settings were used in running the standard gas calibration mixture supported the assumption made in the conversion of 1° to 2° CF that there is a direct linear relationship between peak height and sensitivity setting, the standard errors being very small even though the values represent the mean conversion factor for all the range and attenuation settings for the reported concentration. Oxygen was contained in a second calibration mixture, and was not accurately calibrated until August 1983. Until then it was 'calibrated' roughly using air, in which it was assumed that there was 20% (200 000 vpm) O_2. This is now known to have led to oxygen concentrations being underestimated by ≤8%, approximately.

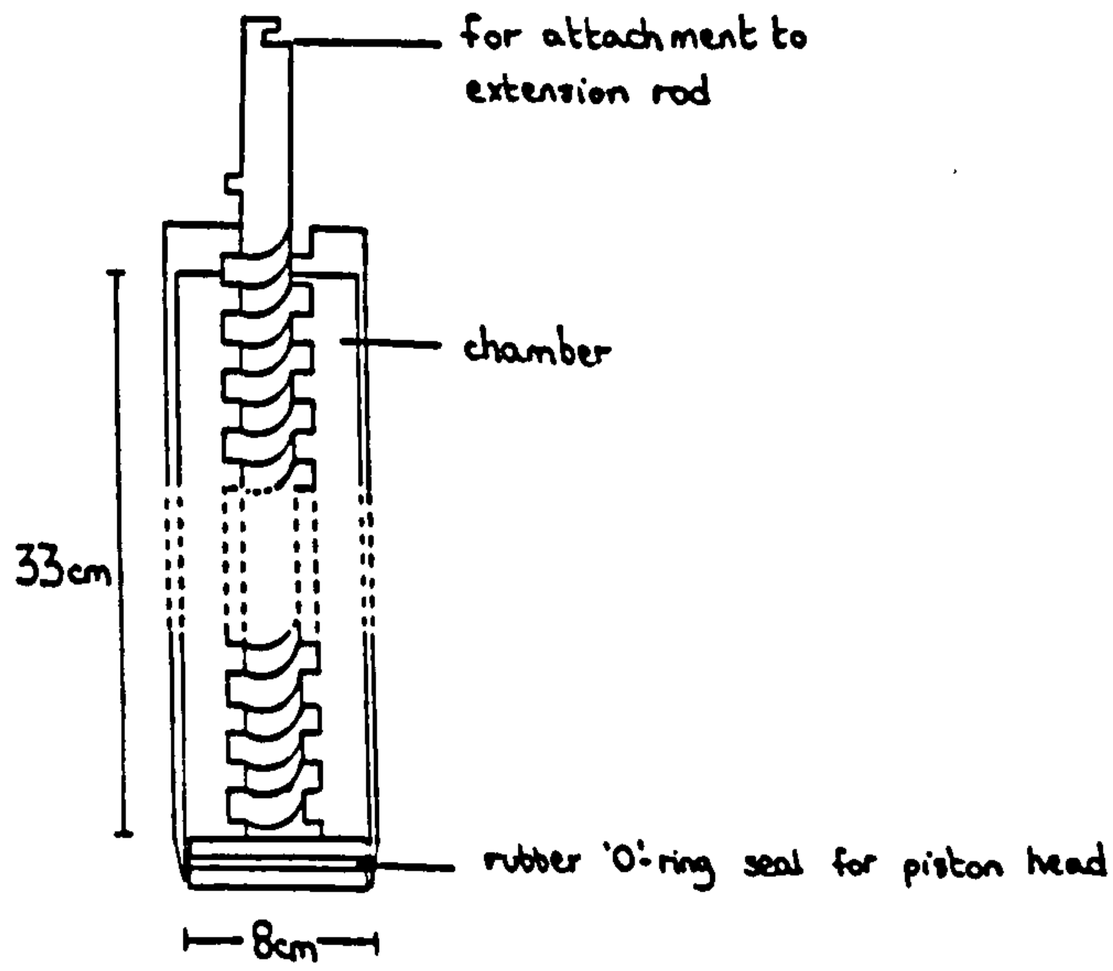
APPENDIX E. MEASUREMENT OF GAS DIFFUSION THROUGH PEAT

a) Collection of peat cores

Cores of peat down to 1 m were collected from MH using a large steel cylinder with a sharpened lower edge, the entire peat-filled corer being dug out with a spade. The core was then transferred to a 19 cm-diameter PVC storage tube which fitted snugly inside the steel corer.

Cores of peat from deeper down were collected using an 8 cm-diameter stainless steel piston borer attachment fitted to an extension rod with the piston down level with the bottom (sharp) rim of the chamber (Fig. E.1). This was pushed down into the peat until the rim was at the depth at which the top of the core was to start.

FIG. E.1 Piston-borer attachment for use with extension rods



Then, ensuring that the tommy bar was kept at a constant height above the peat surface, it was turned to force the chamber down into the peat, the piston head remaining in its original position, so filling the chamber. To remove the core, the whole apparatus was gently pulled up. More often than not the lower part of the core was left behind, still attached to the peat mass, and in some cases the peat

was so wet that nothing was brought up, but sufficient cores were collected from a range of depths for use in the experiment. These cores were extruded into the experimental glass tubes, of the same diameter as the borer, and capped. In total, 11 cores were collected from depths of 15 cm to 275 cm, all from MH. They were returned to London intact and fully water-saturated, and stored at 4°C until required.

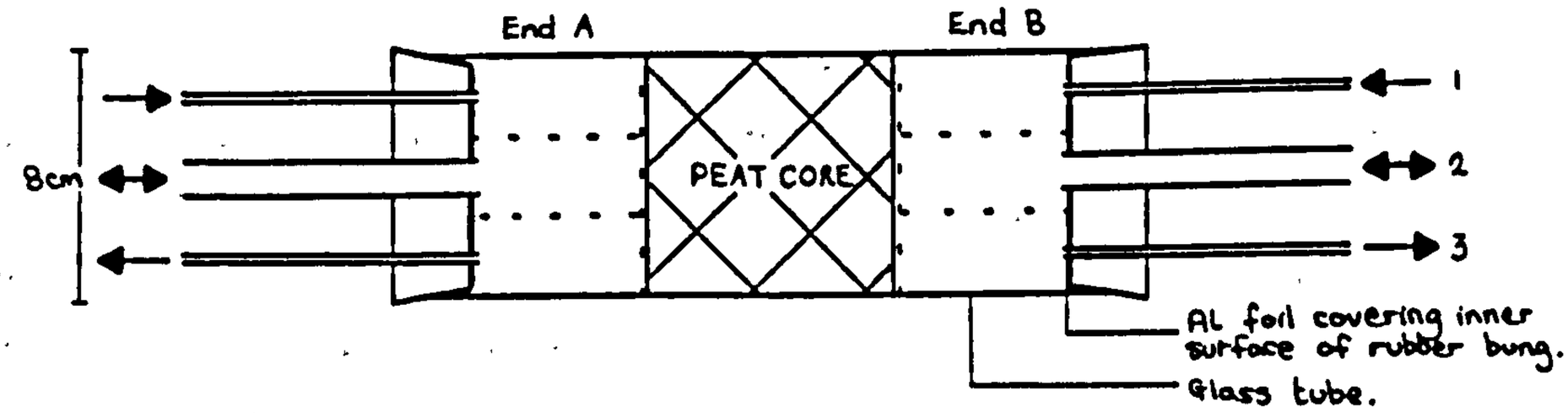
b) Apparatus and preparation of experimental cores

The smaller cores were used directly. Once these experiments had been run, the larger cores were prepared: a smaller core was cut from the centre with a circular metal cutter attached to one end of the 8 cm-diameter glass tube into which the smaller peat core was transferred. The glass tubes were approximately 30 cm long, and in all cases the cores were cut to between 8 and 14 cm and positioned in the centre of the tube. Care was taken to ensure that the core was in contact with the inside wall of the glass tube all the way round, and although a few natural, discrete gas spaces could be seen, as far as could be discerned there were no continuous gas channels linking the gas space at each end. As far as possible, any compaction of the peat was avoided. Plunger-like devices were constructed from punched brass plates to hold the peat in place. They were held in position by a cylinder of punched brass which in turn was held in position by a large rubber bung used to seal each end of the glass tube. The surface of the rubber bung in contact with the gas space was covered with aluminium foil to prevent absorption of gases by the rubber. The apparatus is illustrated in Fig. E.2.

To enable the results to be related to the field peat, the bulk density of each core was determined when the gas diffusion measurements were complete.

The two ends of the glass tube were labelled A and B. At each end three PVC tubes connected the gas space with the exterior. A large tube (7 mm bore) entered in the centre of the bung and was used for the initial evacuation procedure and subsequent filling and emptying of the gas space with water; two smaller tubes (1 mm bore) entered opposite one another towards the edge of the bung and were used for the introduction and withdrawal of gases. The wide tubes

FIG. E.2 Apparatus for measuring gas diffusion rates through peat



1. Small inlet tube, I.D. 1mm (gas in)
2. Large tube, I.D. 7mm (water in and out)
3. Sampling tube, I.D. 1mm (gas sample out)

were sealed by a screw-gate (Hoffman) clamp, the narrow tubes with 3-way taps.

During manipulation some of the peat water was lost from the peat core, so it was necessary to try and resaturate it in order to avoid an overestimate of diffusion rate. This was done by positioning the tube vertically, totally filling the lower gas space and partially filling the upper with water, attaching the upper end large tubing to a Büchner flask and evacuating. Whilst evacuation of the core was in progress, water was drawn up into it from below. On gradual restoration of the pressure, water moved in from the upper space. By repeating this procedure several times the core became waterlogged, though some discrete gas spaces could still be seen. Both ends of the tube were then filled with water and the apparatus was left overnight in an incubator at 20°C to allow the temperature of the peat and water to equilibrate. All the diffusion experiments were carried out at 20°C, despite the field temperature being approximately 5°C, to reduce the time needed to complete any experiment.

c) Experimental design and procedure

Initially it was planned to stop the production of gases within the peat core by killing the micro-organisms responsible. Autoclaving the peat was attempted but the increased pressure detroyed the integrity of the core and resulted in significant changes to its structure. Microbial inhibitors were dismissed because of the

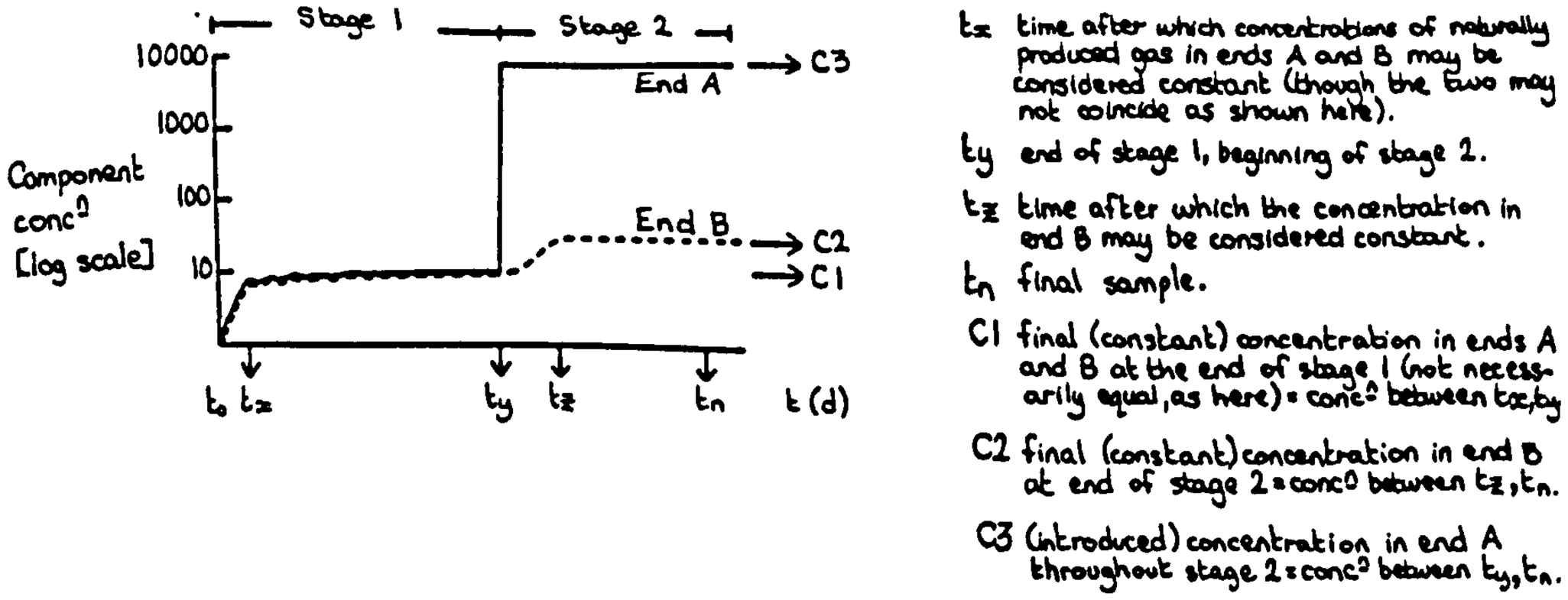
difficulty of ensuring that such a dense medium as peat had been thoroughly treated, and also because with this method there are inherent risks of unwanted chemical interference with the relatively poorly understood mechanisms of anaerobic microbial respiration and its various products when applied to a 'complete' natural medium rather than a pure laboratory culture of known composition. Another technique, gamma irradiation, was prohibitively expensive. Hence, diffusion experiments were designed to involve two separate stages. In the first stage (after overnight temperature equilibration) both ends of the glass tube were filled with N_2 by displacing the water. A 24-hour sampling period had been established as being short enough to prevent any significant change in concentration gradient across the peat core during stage II. The first 5 cm^3 withdrawn was expelled and a further 25 cm^3 was taken for analysis. Both ends were then filled with water and this was immediately displaced with N_2. In this way it was possible to ensure that the entire gas space was filled with N_2 at the beginning of each sampling period. Between samples the glass tube was replaced in the incubator. This initial stage, with N_2 and 24-hour sampling, was continued until a baseline rate of gas evolution from the core had been established. At this point stage II was initiated. After taking the final stage I samples, the ends of the glass tube were again filled with water, but while end B was refilled with N_2, end A was filled with the required concentration of CH_4 or CO_2, or both. A sample was taken immediately from both ends and this small volume (20 cm^3, $\simeq$ 5% of gas space volume) was replaced with N_2. Further samples were taken every 24 hours from both ends of the tube. Theoretically, for the subsequent calculation to hold, the concentration gradient across the peat core must remain constant, but in practice this is not possible since gas will move down the concentration gradient immediately this is set up, and thus the gradient will change continually. For practical purposes, therefore, it was aimed to make the sampling period short enough to ensure that the concentration gradient did not change by more than 10% and, after sampling, the original concentrations were replaced in both ends, so reinstating the initial concentration gradient and effectively keeping

it 'constant'. Using the notation given in Fig. E.3, and assuming the core length, l, is constant,

$$\frac{C2 - C1}{C3 - C1} \times 100 < 0.10$$

for the calculation to give worthwhile results. The concentration in both ends of the glass tube should be constant in order for the concentration gradient to be calculated accurately. Again, 'constant' was taken as <10% difference between the maximum and minimum concentrations measured.

FIG. E.3 Theoretical results for methane and carbon dioxide from peat gas diffusion experiment



The rate of gas evolution from the core during stage II was thus calculated once it had stabilised and, given the baseline evolution rate measured in stage I, the net rate of evolution from the core could be calculated (Fig. E.3).

For each experiment three tubes were set up, including one control tube in which no experimental gases were introduced into end A, that is, the control gave a continuous measure of the baseline rate of gas evolution throughout stages I and II of the experiment. A number of different cores were used, representing peat from different depths down the profile, and different concentrations of experimental

gases were introduced to measure the effect on the diffusion rate. The results are given in Chapter 4.

APPENDIX F. SULPHIDE, IRON AND HYDROGEN ION CHEMISTRY AS APPLICABLE TO ACID PEAT, AND THE ADOPTED METHOD OF MEASUREMENT OF TOTAL SULPHIDE CONCENTRATION THEREIN

a) Introduction

The supply of oxygen to a peat system is limited by its diffusion rate in water. Oxygen is supplied from the air and in many of the products of peat decay, but the demand for it in the peat exceeds the rate at which it can be replenished (there is a 10^4-fold drop in the diffusion rate of O_2 in water compared with that in air). Hence any available oxygen is very quickly used, and the bulk of peat more than a few centimetres below the surface exists under reducing conditions. Sulphur is present in its sulphide (S^{2-}) form and iron mostly in its ferrous (iron II) form. Both S^{2-} and Fe^{2+} exist in equilibria, and the positions at which these will stabilise depend on local (chemical) conditions in the peat and the complex inter-relations of the chemical species present. Iron (II) and sulphide ions exist in equilibrium systems of their own, but the equilibria are related through H_2S and H^+ ion concentrations. Very simply,

$$FeS + 2H^+ \Leftrightarrow Fe^{2+} + H_2S$$

$$\text{and} \quad H_2S \Leftrightarrow HS^- + H^+ \Leftrightarrow S^{2-} + 2H^+.$$

This is obviously a gross simplification, but clearly the position of the equilibria is sensitive to the local pH.

b) Calculation of the position of H_2S equilibrium in peat

The redox potential reading, E (mV), made in the field was converted to total S^{2-} concentration using a calibration curve. The sulphide calibration standards and the measurement of the field sample were both carried out in the presence of SAOBII (see text for details), i.e. at a high, constant, pH. Thus, the position of the sulphide solution equilibrium will be different from what it had been in the peat before the buffer was added to the sample. The electrode measured total sulphide concentration in solution, and to determine what proportion of this was originally present in the peat as H_2S, HS^- and S^{2-} the pH of the peat is used (i.e. to determine the position of the equilibrium in the peat from which the sulphide solution

originated). In other words, if the concentrations of each species present in the peat are described by

$$[H_2S] = a[S_t]$$
$$[HS^-] = b[S_t]$$
$$[S^{2-}] = c[S_t]$$

where $[S_t]$ is the total sulphide concentration in the solution (measured by the electrode), the *proportion* of each is represented by the conversion factors (proportionality constants) a, b and c. The value of the constants will change with the pH of the solution. The derivation of the general form of the three conversion factors is shown below.

$H_2S \Leftrightarrow H^+ + HS^-$ 1 $K_1 = 1 \times 10^{-7}$

$HS^- \Leftrightarrow H^+ + S^{2-}$ 2 $K_2 = 1 \times 10^{-13}$

$H_2S \Leftrightarrow 2H^+ + S^{2-}$ 3 $K = 1 \times 10^{-20}$

$$K_1 = \frac{[H^+][HS^-]}{[H_2S]} = 1 \times 10^{-7} \quad 1$$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = 1 \times 10^{-13} \quad 2$$

$$K = K_1K_2 = \frac{[H^+]^2[S^{2-}]}{[H_2S]} = 1 \times 10^{-20} \quad 3$$

Let $[S_t^{2-}]$ be the (measured) total sulphide concentration in the system

$$[S_t^{2-}] = [H_2S] + [HS^-] + [S^{2-}]$$

To calculate $[H_2S]$ in the peat,

from 1

$$[HS^-] = \frac{K_1[H_2S]}{[H^+]}$$

from 3

$$[S^{2-}] = \frac{K_1K_2[H_2S]}{[H^+]^2}$$

$$\therefore [S_t^{2-}] = [H_2S] + \frac{K_1[H_2S]}{[H^+]} + \frac{K_1K_2[H_2S]}{[H^+]^2}$$

$$= [H_2S]\left\{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right\}$$

$$[H_2S] = [S_t^{2-}] \Big/ \left\{1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right\}$$

APPENDIX F

To calculate $[HS^-]$ in the peat

from 1

$$[H_2S] = \frac{[H^+][HS^-]}{K_1}$$

from 2

$$[S^{2-}] = \frac{K_2[HS^-]}{[H^+]}$$

$$\therefore [S\tilde{t}^-] = \frac{[H^+][HS^-]}{K_1} + [HS^-] + \frac{K_2[HS^-]}{[H^+]}$$

$$= [HS^-]\left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right\}$$

$$[HS^-] = [S\tilde{t}^-] \Big/ \left\{1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right\}$$

To calculate $[S^{2-}]$ in the peat

from 3

$$[H_2S] = \frac{[H^+]^2[S^{2-}]}{K_1K_2}$$

from 2

$$[HS^-] = \frac{[H^+][S^{2-}]}{K_2}$$

$$\therefore [S\tilde{t}^-] = \frac{[H^+]^2[S^{2-}]}{K_1K_2} + \frac{[H^+][S^{2-}]}{K_2} + [S^{2-}]$$

$$= [S^{2-}]\left\{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right\}$$

$$[S^{2-}] = [S\tilde{t}^-] \Big/ \left\{1 + \frac{[H^+]}{K_2} + \frac{[H^+]^2}{K_1K_2}\right\}$$

From these three equations relating the concentration of each species in the equilibrium with the total sulphide concentration and the pH, it is possible to calculate the shift in the equilibrium with pH (see Table F.1).

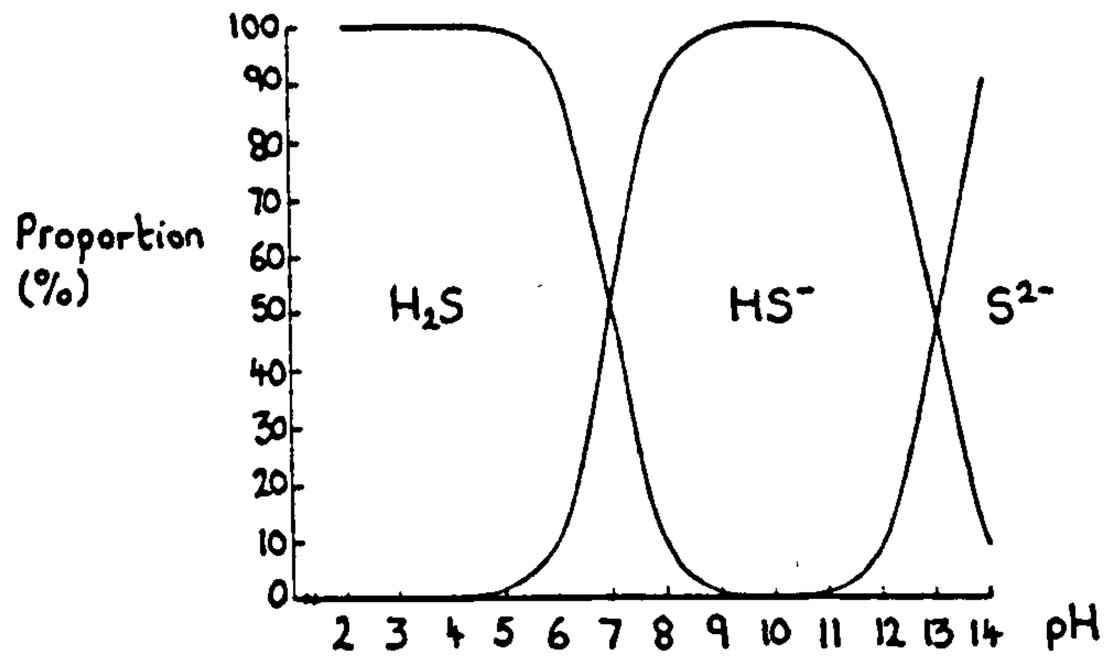
Thus, in a solution of sulphide at around pH 3-5, as is generally the case in the blanket peat under consideration, between 99.0 and 99.9% of the total S^{2-} in the system is in the form of H_2S, about 1.0 to 0.01% is as HS^-, and virtually none (1.0×10^{-12} to 1.0×10^{-8}%) is as S^{2-} (see Fig. F.1). At the pH of the peat, then, $[H_2S] \approx 100\%$, as is free $[S^{2-}]$ at the time and conditions of measurement. So, the measured pS was equated with the field $[H_2S]$ throughout.

APPENDIX F

TABLE F.1 pH dependence of sulphide species' proportions in solution

pH	$[H_2S]$ (%)	$[HS^-]$ (%)	$[S^{2-}]$ (%)
2	99.9	1.0×10^{-3}	1.0×10^{-14}
3	99.9	1.0×10^{-2}	1.0×10^{-12}
4	99.9	0.1	1.0×10^{-10}
5	99.0	1.0	1.0×10^{-8}
6	90.9	9.1	1.0×10^{-6}
7	50.0	50.0	1.0×10^{-4}
8	9.1	90.9	9.1×10^{-4}
9	1.0	99.0	9.9×10^{-3}
10	0.1	99.8	0.1
11	9.9×10^{-3}	99.0	1.0
12	9.1×10^{-4}	90.9	9.1
13	5.0×10^{-5}	50.0	50.0
14	9.1×10^{-7}	9.1	90.9

FIG. F.1 Effect of pH on proportion of total sulphide present in solution as H_2S, HS^- and S^{2-}



c) Position of FeS equilibrium in peat

Similarly, kinetics can be used to calculate the expected amount of FeS in peat at a given pH, if the concentration of H_2S is known.

$$FeS + 2H^+ \Leftrightarrow Fe^{2+} + H_2S \qquad K_{FeS}$$

$$FeS \rightarrow Fe^{2+} + S^{2-} \qquad K_3$$

$$S^{2-} \rightarrow H_2S \qquad K_4$$

where $K_{FeS} = K_3K_4$

$K_3 = K_{sp}FeS$, the solubility product constant for FeS

$= 1 \times 10^{-17}$

and K_a = the reversed acid dissociation constant for H_2S

$= 1 \times 10^{20}$

So, $K_{FeS} = (1 \times 10^{-17}) \times (1 \times 10^{20})$

$= 1 \times 10^{3}$

Since K_{FeS} is large, the reaction will proceed with ease, and in acid conditions the FeS precipitate will redissolve, giving Fe^{2+} and H_2S.

d) Selectivity of the Ag/S electrode and the nature of the measurements made with it

Profile measurements allowed quantification of sulphide species. H_2S is produced by various pathways in reducing conditions. In solution it exists as an equilibrium of sulphide species:

$$\left.\begin{array}{ll} H_2S \Leftrightarrow HS^- + H^+ & K_1 = 1 \times 10^{-7} \\ HS^- \Leftrightarrow S^{2-} + H^+ & K_2 = 1 \times 10^{-13} \end{array}\right\} K = 1 \times 10^{-20}$$

In an acid solution, such as peat, dissociation of the H_2S is minimal, the high $[H^+]$ keeping the equilibrium over to the left. The exact proportion of the total S^{2-} concentration present as free S^{2-} ions, as HS^- and as H_2S is therefore dependent on the pH.

The Ag/S electrode solid state membrane sets up a potential when in contact with (free) S^{2-} ions. Thus, the electrode potential, E (mV), is proportional to the activity of the free S^{2-} ions, and will not register those complexed with H^+ as either HS^- of H_2S. SAOBII is added to the standard solution or the sample to be measured to free all S^{2-} ions by complexing with the H^+ (EDTA), so when the electrode was used it was responding to the *total* S^{2-} activity which was all in the form of free S^{2-} in the buffered standard or sample (though not in the peat). The ascorbic acid in the SAOBII is a strong reducing agent and thus prevents the oxidation of S^{2-}. The NaOH in the SAOBII provides a high and constant ionic strength so that the concentration of S^{2-} ions is roughly equivalent to their activity. It effectively pushes the pH of the solution in which the sulphide is being measured to the high end so that the sulphide solution equilibrium is pushed well to the right (i.e. full dissociation of H_2S to S^{2-} and H^+).

The measured potential was converted to sulphide concentration ($[S^{2-}]$, pS or ppm S^{2-}) using a calibration curve drawn up for the E values of known sulphide (Na_2S) standards prior to each batch of

samples. See Appendix H for details of the calculations involved. This gave total S^{2-} concentration. To calculate the proportion of the total which was initially present as H_2S, HS^- and S^{2-} chemical kinetic methods were used (see above).

APPENDIX G. GARDEN AND FIELD WEATHER PATTERNS

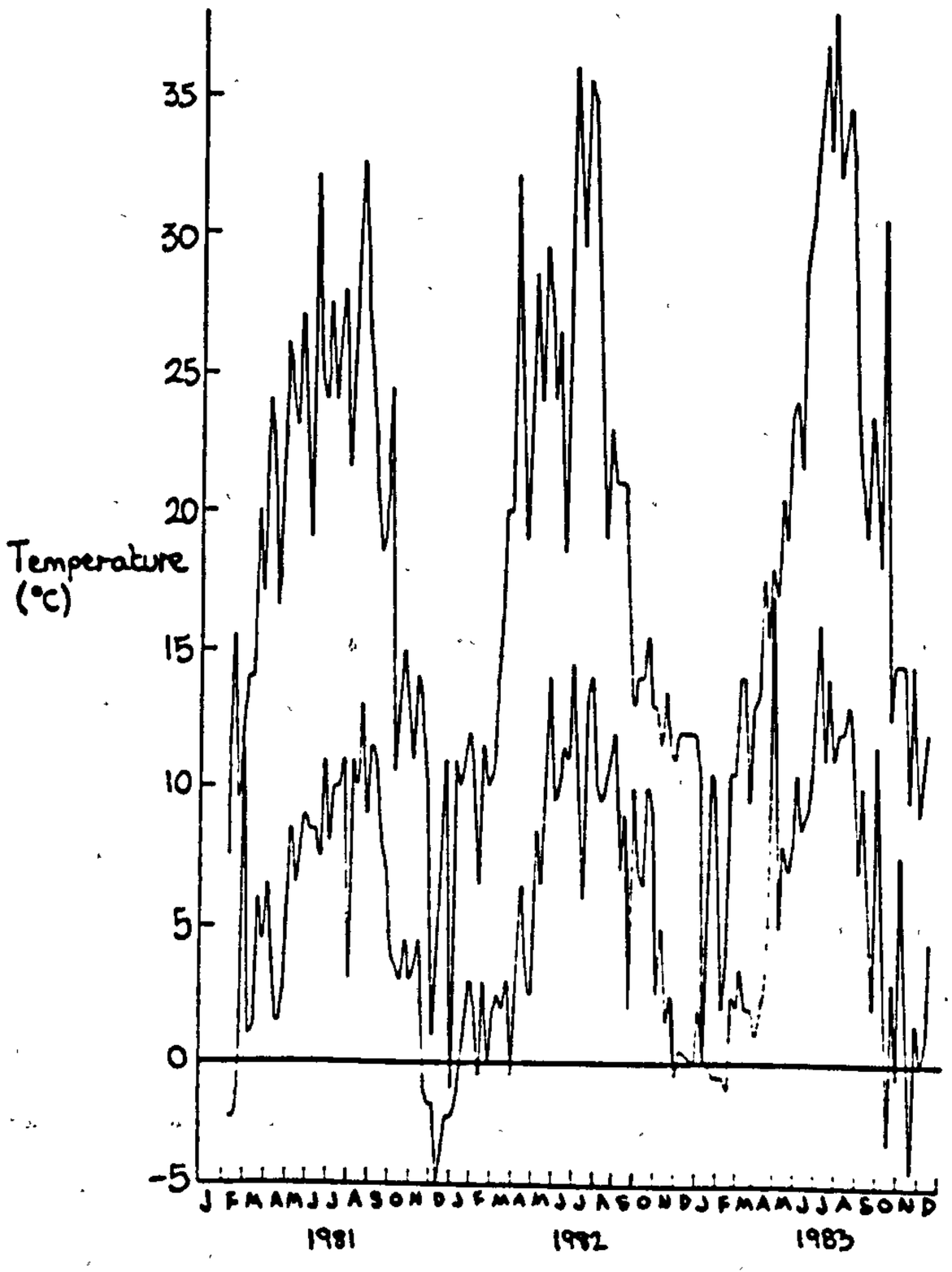
a) Surface weather patterns

Fig. 4.2 shows the weekly mean garden air temperature (at +30 cm above Minibog 2) measured in the morning (0800h-1000h) and early afternoon (1230h-1400h). Means are calculated from five to seven values. The maximum weekly mean was slightly higher in each successive year of the study, though it is possible that the absolute (high) temperatures may be overestimates. Despite efforts to ensure that the bulb of the thermometer was shielded from direct solar radiation, weekly means of 30-35°C seem unlikely. However, the pattern of successive annual increase is supported by data from 30 cm below the peat surface (see below). Fig. 4.2 shows a larger diurnal temperature change in the summer months, of about 10-15°C, compared to about 1-3°C in the coldest periods of the year. It is possible that both ranges are slightly underestimated, since temperatures were recorded between 0800h and 1400h each day and therefore missed the lower night temperatures. The highest summer weekly maxima occurred in July or August. In both complete winters of the study (1981-2 and 1982-3) the daytime temperature rose in January markedly above its sub-zero minimum, but fell back to around freezing in February. In 1982 these low temperatures persisted well into March. February was a consistently very cold month in all three years, but the absolute minimum temperature occurred in different months each winter. In 1981-82 the minimum weekly mean temperature recorded was -3°C (Jan 1982), and the December temperature was also below freezing (-2°C). In 1982-83 February gave the minimum value (≈0°C), and up to the end of December 1983, November was the coldest month, -1.5°C being recorded in the third week. The mean air temperatures (1230h-1400h) for each of the three study years were 12.2°C (1981), 12.9°C (1982) and 12.0°C 1983, giving an overall annual mean air temperature for the garden of 12.4°C.

Fig. G.1 shows the weekly mean maximum and minimum temperatures of the minibog M2 peat-air interface, calculated from daily measurements made for each 24h period and recorded between 0800h and 1000h. The pattern of temperature changes is similar to that of the air temperature, but it should be remembered that the absolute values

in Figs. 4.2 and G.1 are not directly comparable. As in Fig. 4.2, the accuracy of the very high temperatures shown in Fig. G.1 is questionable. The maximum and minimum thermometer was placed on the moss ground layer, with the bulb downwards and the plastic back of the

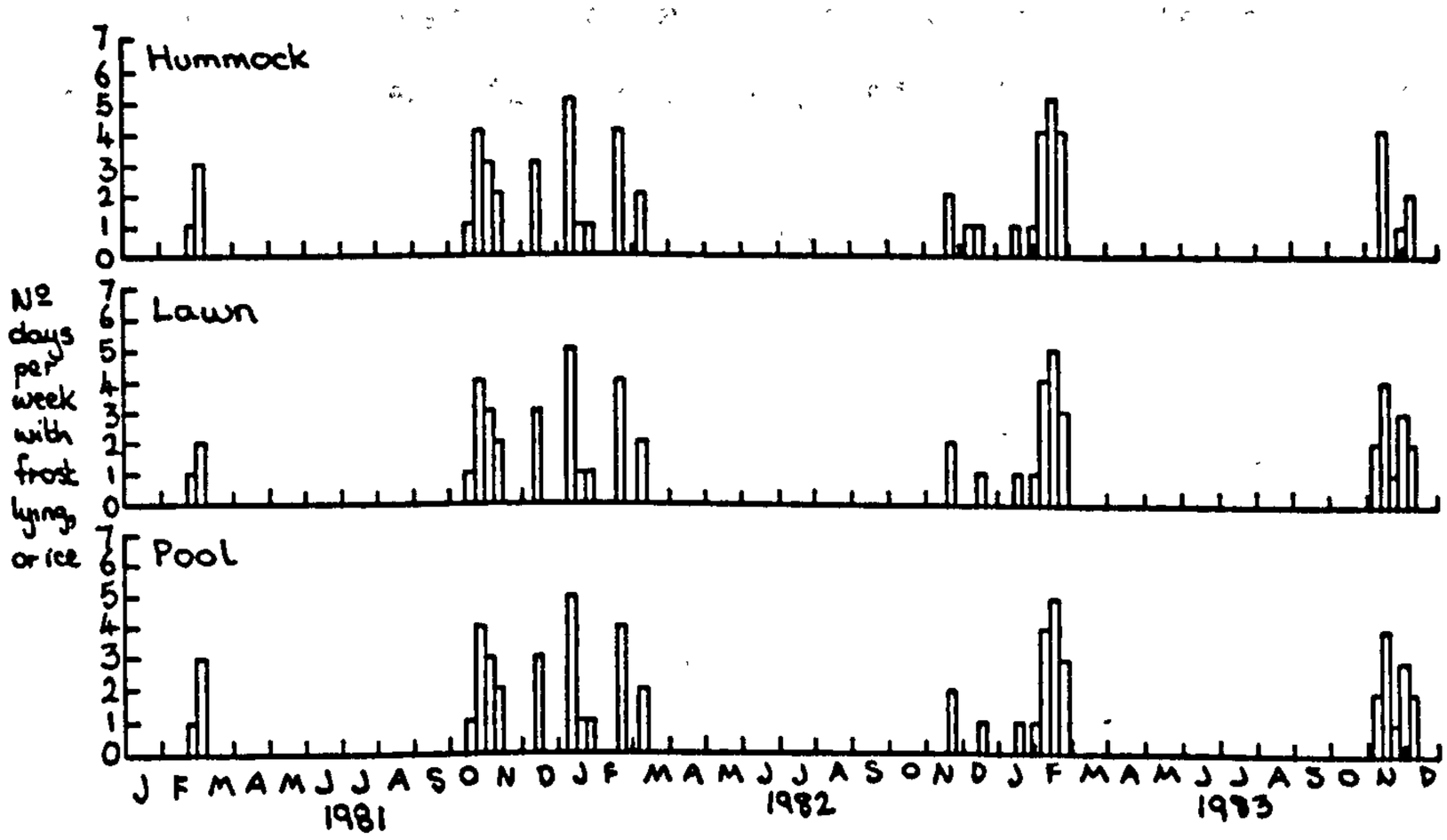
FIG. G.1 Garden peat-air interface temperature, 1981-1983. Weekly mean maximum and minimum temperature, Minibog 2, at 0 cm, 0800h-1000h



thermometer shaded (apparently) from direct sun, but it is likely, in view of the results, that the shading was insufficient. Indeed, on occasions the plastic back of the thermometer was appreciably warm. The mean maximum range of temperature over a 24h period in summer was about 20°C, and in winter between about 5° and 10°C.

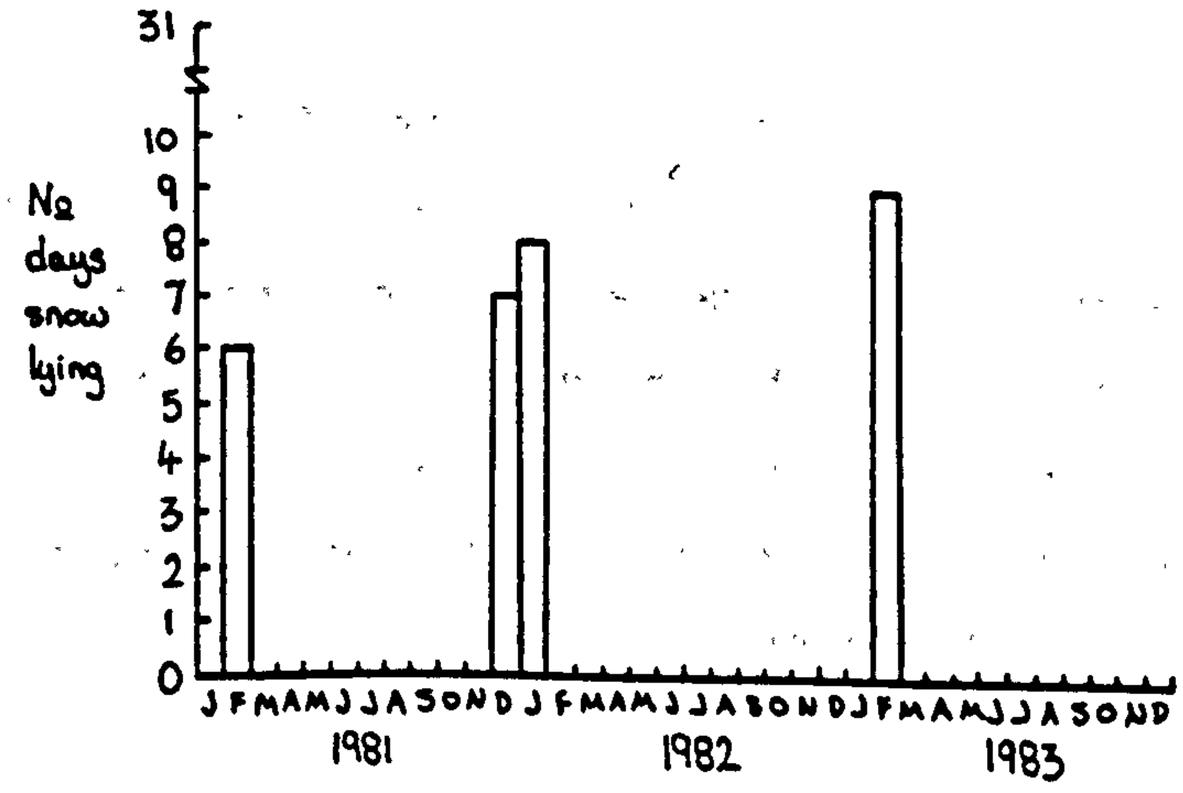
Turning from temperature data to a consideration of other weather variables, Fig. G.2 shows the number of days per week that ground

FIG. G.2 Occurrence of ground frost in garden plot, 1981-1983



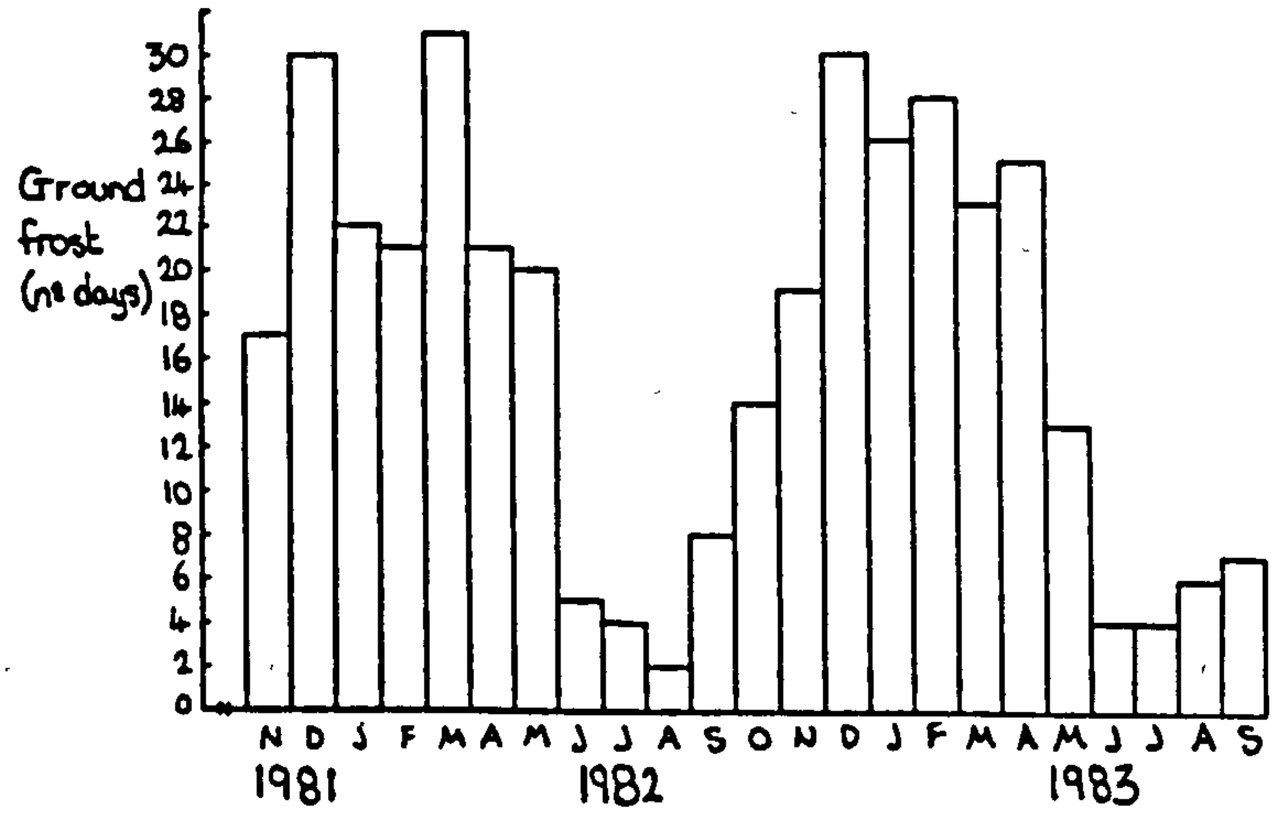
frost was recorded (as rime, frozen surface vegetation or pool water) in the garden. Frost days occurred between mid-October and mid-March in 1981-82, but not until mid-November in the two following winters, and in 1981-82 they ended in March. Fig. G.3 shows the number of snow-days per month in the garden for the study period.

FIG. G.3 Days with snow lying in garden plot, 1981-1983



Meteorological Office (Met. Off.) data indicated that there was no month of the year at MH when ground frost did not occur (Fig. G.4). Between November and March ground frost was present on over half the days of the month. Unfortunately, similar data were not available for

FIG. G.4 Occurrence of ground frost at Moor House, 1981-1983

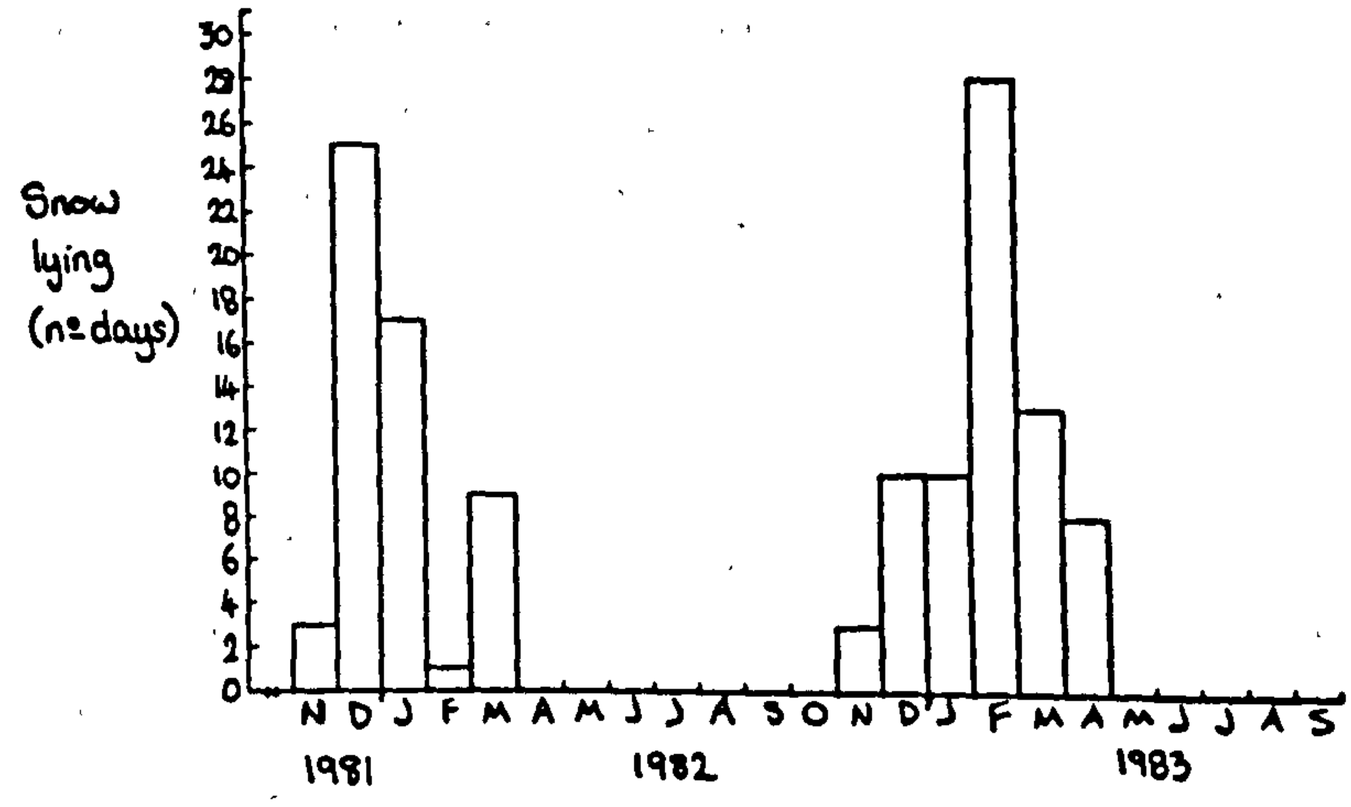


CR, but field notes (made around 1000h) recorded ice on the wet lawn areas in December 1981, in October and December 1982 and in April 1983. At MH snow lay for at least one day between November and March in both winters 1981-82 and 1982-83; in 1982-83 the snow persisted into April (Fig. G.5), and the mean number of days per month (with snow) with snow lying was 12, compared with 10 for 1981-82. The distribution of snow-days also varies, being mire erratic in 1981-82 than in 1982-83. In 1981-82 the maximum number of snow-days occurred in December (25), and the minimum in February (1). In 1982-83 December had 10 days of snow lying, the maximum occurring in February (28) and the minimum in November (3).

Fig. G.6 shows the total weekly precipitation in the garden for 1981-83. The wettest year of the study was 1982, with a total annual precipitation of 560 mm, compared with 325 mm and 475 mm in 1981 and 1983, respectively. The mean total weekly precipitation for the three study seasons was 7 mm, 13 mm and 8 mm for 1981, 1982 and 1983,

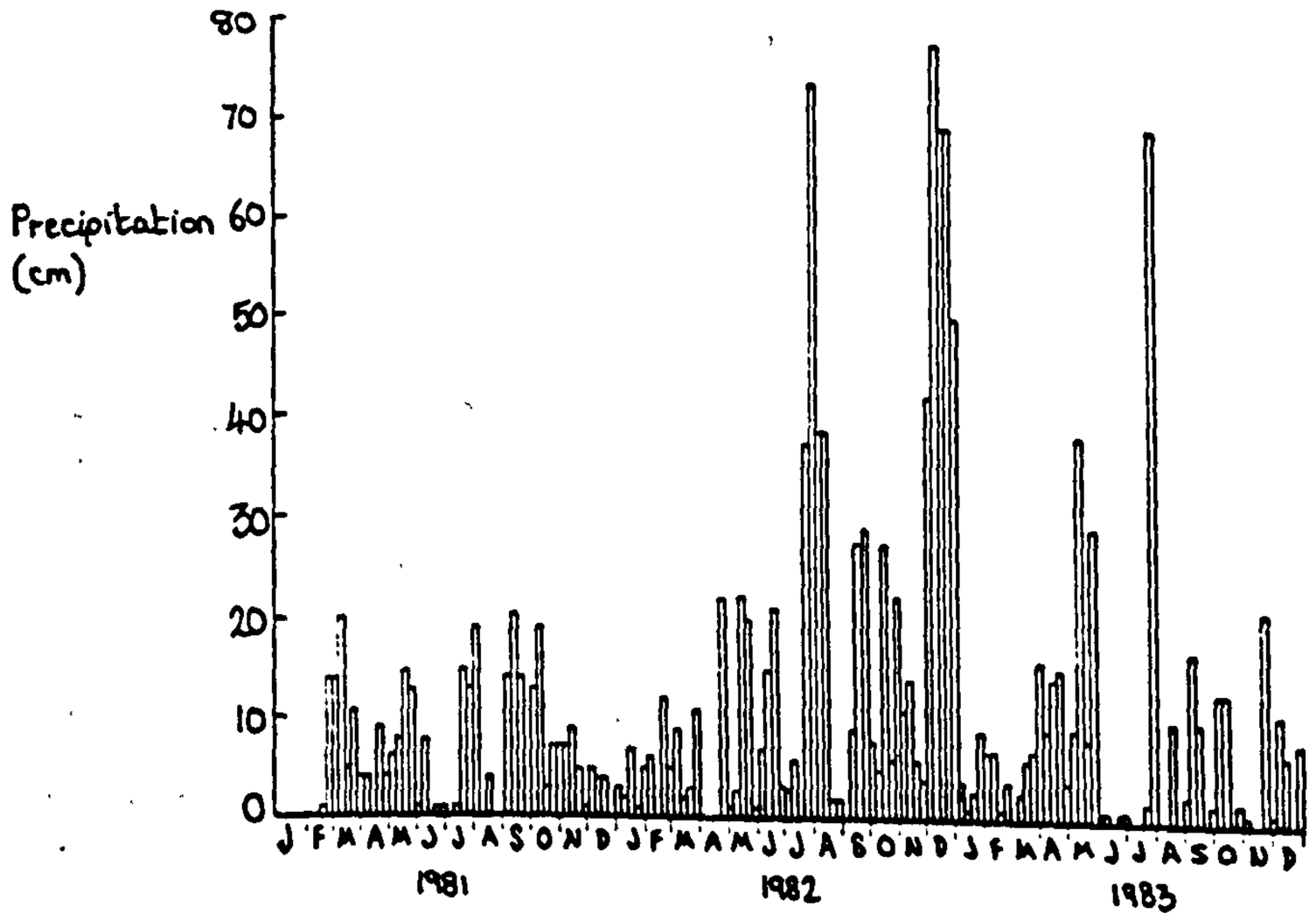
APPENDIX G

FIG. G.5 Days with snow lying, Moor House, 1981-1983



respectively, the precipitation being more evenly distributed over the year in 1981 than in either of the other two years. In 1983 the rainfall pattern was rather erratic. In 1982 exceptionally wet periods in late July to early August and in December contributed significantly to the annual total. In these periods the mean weekly precipitation was 43 mm and 47 mm, respectively, the latter partly

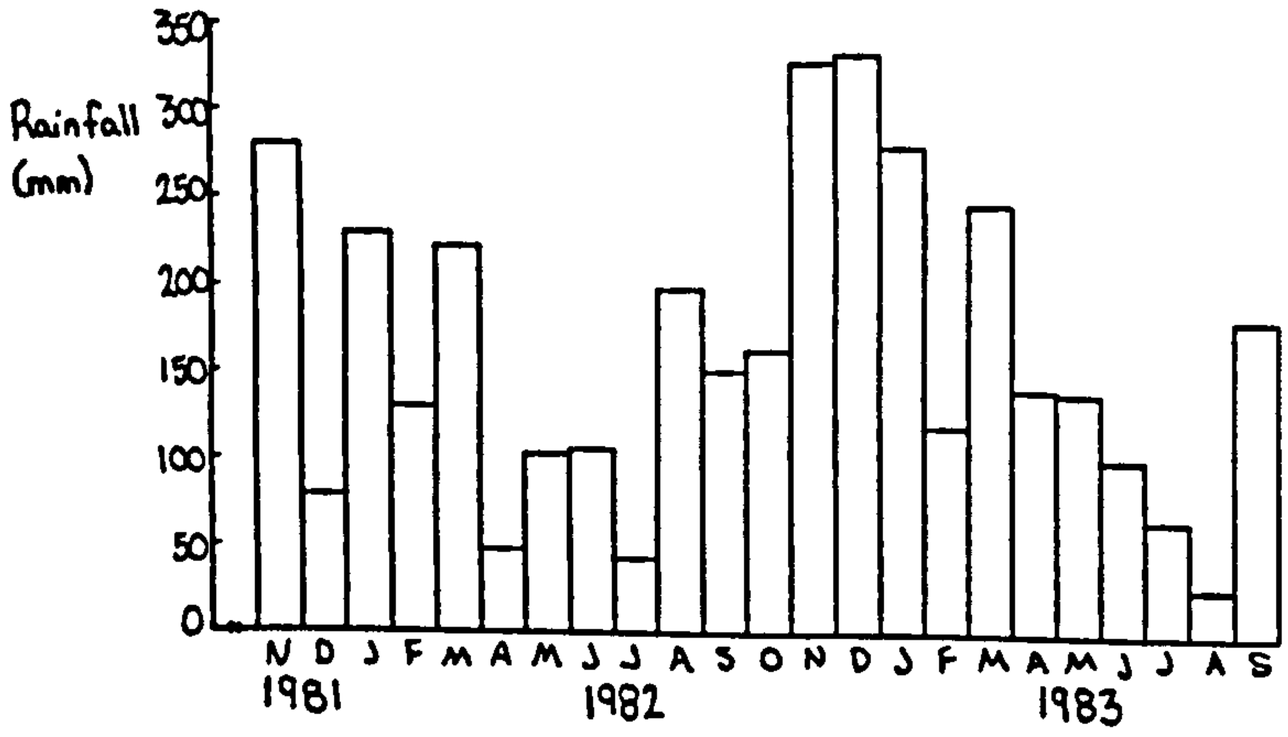
FIG. G.6 Garden plot precipitation, 1981-1983



being attributable to snow-melt. In 1983 there were three distinct weeks of heavy rainfall; two in May and one in July similar to the wet July week the previous year, but 1983 also had the highest number of weeks with less than 1 mm of rain (11 compared with 8 and 7 in 1981 and 1982, respectively). In 1981, the wettest March in 30 years occurred. Over the garden plot a total of 57 mm fell, compared to the more usual 25 mm and 19 mm recorded in the following two years.

Total monthly rainfall at MH (Met. Off. data) is shown in Fig. G.7. The August 1983 total is likely to be an underestimate because the rain gauge was disturbed. The total annual rainfall for the three study years, 1981-83, was 1931 mm, 2049 mm and 1833 mm, respectively, and is roughly 4- to 6-fold that in the garden plot (which includes snow-melt). Thus, of the two field seasons in which gas samples were

FIG. G.7 Moor House rainfall, 1981-1983.
Met. Off. data.



collected, 1983 was slightly wetter than 1982; the mean monthly rainfall was 171 mm in 1982 and about 153 mm in 1983. Rain fell in every month, but the distribution was not the same in both years. April to July were the driest months, though in both years rainfall dropped markedly in February but recovered in March. As in the garden plot, there was no consistency as to which was the wettest month or months.

b) **Peat temperature**

Changes with depth (measured)

Peat temperatures at -30 cm in Minibog 2 were recorded simultaneously using a thermometer and a temperature-calibrated thermistor. Theoretically, the thermistor should give more accurate peat temperature measurements because the probe remains in position while the record is made, whereas the thermometer reading will change as the bulb is lifted out of the peat. In practice, the thermistor was found to give occasional erratic results and so corresponding thermometer records were continued throughout the study to act as a check on this. All the data were used to calculate a linear regression of thermistor on thermometer temperatures. Morning and afternoon records were treated separately. The regression equations ($y = 1.2x - 2.2$, $r^2 = 0.80$, $p<0.0001$; and $y = 1.2x - 3.0$, $r^2 = 0.90$, $p<0.0001$, for morning and afternoon data, respectively) indicate no serious discrepancies between the two sets of results. Although the value of the slope represents a difference of 20% between thermometer and thermistor temperature, when the absolute difference between the two is calculated for the extremes of temperature measured by the thermometer at -30 cm (1.0°C and 20.5°C) the differences are between +1.1°C and -2.8°C (thermistor relative to thermometer). An occasional value which may be in error by a maximum of this amount will not affect any final results, which are not of such fine resolution, but are based on mean values. At temperatures around the mean (about 12°C) errors arising are no greater than ±0.6°C.

Changes with depth (predicted)

Daily and annual temperature fluctuations approximate to a harmonic wave function. Assuming the peat concerned to be a semi-infinite slab of isotropic material, and the temperature fluctuations at the peat-air interface to follow a sinusoidal curve, the temperature oscillations in the peat can be described by the equation

$$T(z,t) = T_o + A_o e^{-z/D} \mathrm{Sin}(\omega t - Z/D) \quad \text{(Monteith 1973)} \quad \text{(G.1)}$$

where $T(z,t)$ = temperature at depth Z and time t (°C)
T_o = mean interface temperature (°C)
A_o = amplitude of the oscillations at the interface (°C)

Z = depth below the peat surface (m)
D = the "damping depth"; that is, the depth at which the amplitude of the surface oscillations is reduced to e^{-1}, or 0.37, that at the interface (m)
ω = angular frequency of the oscillation, which evaluates to 2π divided by the length of the oscillation, i.e. $(2\pi h^{-1})/24$ for a daily cycle (t in hours), or $(2\pi d^{-1})/365$ (t in days).

The equation predicts that as the profile is traversed downwards (Z increases) temperature oscillations become damped, that is, their amplitude is reduced, and there is also a shift in the positions of peaks and troughs relative to those at the surface. In equation (G.1), the expression $e^{-Z/D}$ describes the proportion by which the amplitude of the surface oscillations, A_o, is reduced:

$$A_z = A_o e^{-Z/D} \qquad (G.2)$$

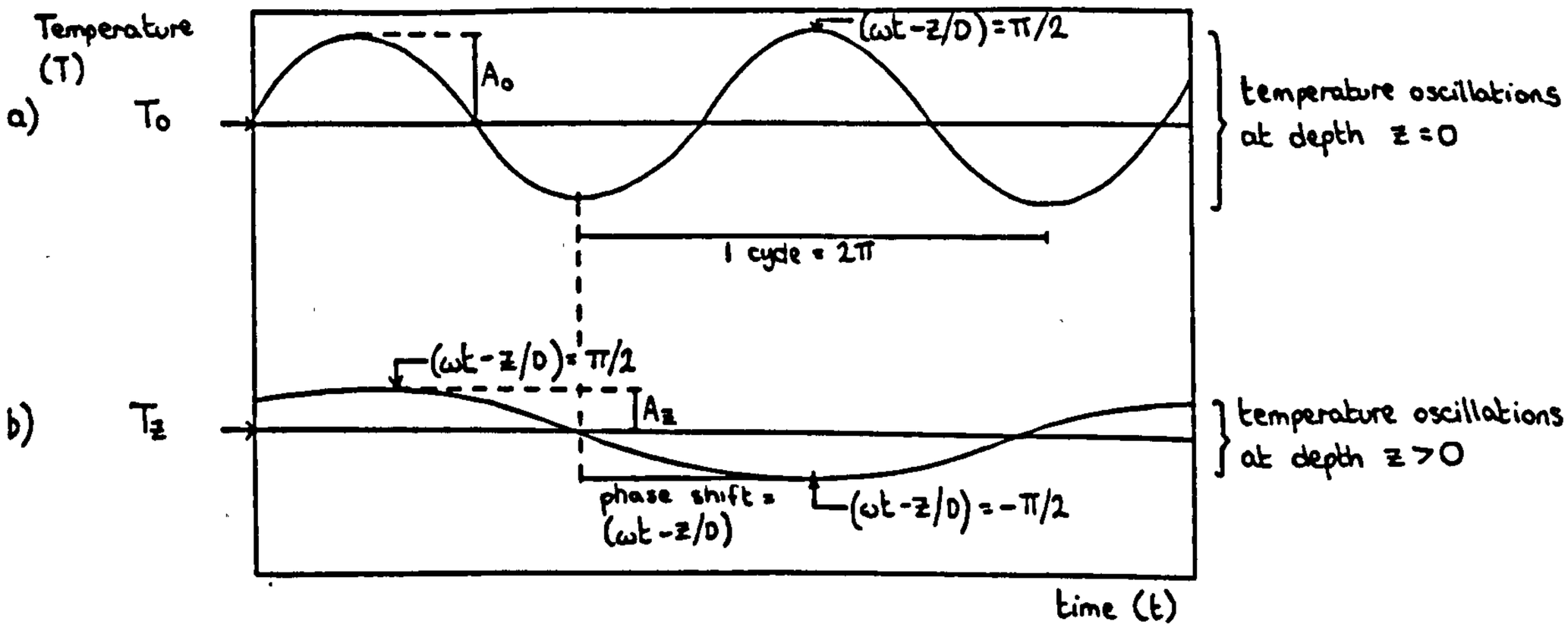
The expression (ωt-Z/D) represents the phase shift, or time lag, before a surface peak, or any other point on the wave, reaches depth Z.

For the interface condition, i.e. at depth Z=0 m, equation (G.1) simplifies to

$$T(o,t) = T_o + A_o \mathrm{Sin}(\omega t) \qquad (G.3)$$

The general form of the equation is illustrated in Fig. G.8.

FIG. G.8 Ideal form of temperature oscillations in a semi-infinite, isotropic medium



Two solutions to the equation $T(z,t) = \bar{T}_o + A_o e^{-z/D} \sin(\omega t - z/D)$.
a) Illustrates the air-medium interface temperature oscillations
b) Illustrates the corresponding temperature oscillations at depth z in the medium. For further explanation, see text.

APPENDIX G

The damping depth, Z=D, is specific for different cycle lengths and is characteristic for a given medium since it is dependent on the thermal properties of the medium. Once known, it can be used to estimate other useful parameters which approximately describe heat movement through the peat:

The rate at which temperature maxima and minima appear to move downwards into the peat is given by ωD, obtained from the expression $(\omega t - Z/D)$ which evaluates to 2π (i.e. $\mathrm{Sin}(0)=2\pi$rad), or -2π, at the maximum and minimum temperatures of the cycle, respectively, for the given values of Z and t.

At depth $Z=\pi D$, the phase angle is π less than that at the surface, that is, the phase shift is 0.5 and the temperature oscillations are exactly out of phase:

$$T_{(0,t)} = T_o + A_o \mathrm{Sin}(\omega t) \qquad \text{Surface (interface) condition}$$

$$T_{(z,t)} = T_o + A_o e^{-z/D} \mathrm{Sin}(\omega t - Z/D) \qquad \text{General form of equation}$$

$$T_{(\pi D,t)} = T_o + A_o e^{-\pi} \mathrm{Sin}(\omega t - \pi) \qquad \text{At } Z=\pi D$$

The effective depth for heat flow can be estimated from $(2D)^{0.5}$ (Monteith 1973). At Z=0 m, the flux reaches a maximum $\pi/4$, or 0.125 of a cycle, before the temperature, i.e. 3 h for a daily cycle or 1.5 months for an annual cycle.

The discussion of peat temperatures which follows includes that based on calculations from the field site data.

The annual damping depth in peat was calculated from equation (G.2), above, using all M2 data collected during the three-year study period. This gave a result of D=40 cm, which was smaller (shallower) than values in the literature. For example Monteith (1973), using data in van Wijk & de Vries (1963), calculates the annual damping depth in peat with 80% (v/v) water content to be about 1 m, and using values derived from Fig. 4 in Bunnell, MacLean and Brown (1975) for the coastal tundra soil at Barrow, Alaska, the annual damping depth evaluates to 1.4 m. So further estimates of D were made using different data sets directly relevant to the present study Sites, for comparison. The results are given in Table G.1. The only year of the

study for which any field measurements relevant to the calculation of D had been made, was in 1981 at the ex-Met. Off. MH weather station,

TABLE G.1 Calculated damping depths in peat for diurnal and annual temperature cycles. Values represent damping depth, D (cm below peat surface). Bold values are derived (see text).

Data source	Present study									*in lit.**	ex-Met.Off. stⁿ data (1981)	
Peat system	Garden				MH			CR		MH	MH	
	M2	P1	L1	H1	P	L	H	site 13	site 17	(H)		
Length of temperature cycle												
Diurnal, D_d	2,1	2,7	3,0	2,2	3,4	2,4	1,8	2,1	1,8	-	4,2	1,3
Annual, D_a	40	51	57	43	65	46	34	40	34	7†	80	24

* Smith, R,A,H, (undated) (see below)

Notes - possible sources of error in the calculated values

D_a=80 A_o based on *minimum* grass temperatures, A_z based on 'earth temperature' amplitude at -30 cm

D_a=24 A_o based on amplitude of air absolute maximum and minimum (height not recorded, but probably +1,5 m), A_z based on 'earth temperature' amplitude at -30 cm

D_a=7 A_o based on 10-year mean above-ground amplitude (height not recorded, but probably +1,5 m), A_z based on 1 year's data, 6 cm below hummock surface

D_d=3,4
D_d=2,4
D_d=1,8 } A_o based on 2-day sampling period maximum and minimum. Data from April-September only (n=5)

D_d=2,1 A_z based on spot temperatures at -5 cm, not daily ranges

D_d=1,8

and these were not ideal. A record of surface temperatures from which A_o could be calculated was not available, and a first calculation, based on the amplitude of *minimum* grass temperatures yielded a value of D=80 cm. A second calculation in which A_o was taken as equal to the amplitude of the absolute air maximum and minimum temperatures (height above the surface was not recorded, but was probably Stevenson screen height of 1.25 m) gave D as 24 cm. In both cases A_z was taken as 5.15°C, the amplitude of the 'earth temperature' at -30 cm. The type of soil in which the 'earth temperature' data were measured was not recorded, but a soil map of the MH NNR (in Smith, undated) shows the area adjacent to the house itself to be of red-brown limestone soils. Thus, there are a number of sources of potential error in these calculations. It is difficult to be sure how the reduction of

organic matter and water content, relative to peat, would change the damping depth, because of the opposing effects of increased thermal conductivity and decreased thermal capacity. If the surface temperature amplitude has been overestimated, this will lead to an underestimate of the damping depth calculated in the second instance. A reasonable estimate of the peat annual damping depth probably lies somewhere between the two values, at about 60 cm. The value of 7 cm was calculated from data in Moor House Occasional Paper No. 4 (Smith, undated): 10-year (1961-70) mean monthly maxima and minima were used to calculate the annual above-ground temperature amplitude, but there was no record of at exactly what height above the ground the measurements were made (though it was probably 1.25 m). This will be a possible source of error in the calculation, although a linear regression calculation of M2 interface (0 cm) temperature (y) on garden air temperature at +30 cm (x) (n=123, data from all seasons) gave $y = 1.1x + 0.4$, suggesting that no great error is likely to arise by equating air and air-peat interface temperatures. Another possible source of error is in the derivation of the sub-surface temperature amplitude, which was calculated from data read from a graph (Fig. 3b in Smith, undated) illustrating one year's temperature fluctuations 6 cm below the surface of a hummock. The (7 cm) result seems unacceptably low (shallow).

It was not possible to calculate the annual cycle damping depth from data collected for the present study since reliable records of sub-surface temperatures were not available over a year-long period. Values have been derived from the daily damping depth, which it was possible to estimate (see below), using the expression $D_a = D_d \times (365)^{0.5}$ (where D_a is the annual damping depth and D_d that of the daily cycle) and are shown in bold in Table G.1).

(The equation used is derived by expressing D_a and D_d in terms of the angular frequency of the oscillation, ω, as in Monteith's equation 8.16:

$$D = (2K/\omega)^{0.5}$$

where K = the thermal diffusivity of still air.

Evaluating ω_a and ω_d, both with the period of oscillation in days, and substituting the values into the above equation gives

$$D_a = (2K/(2\pi/365))^{0.5}$$

$$\text{and} \quad D_d = (2K/(2\pi/1))^{0.5}.$$

After rearrangement to

$$D_d = (2K)^{0.5}/(2\pi)^{0.5}$$

$$\text{and} \quad D_a = ((2K)^{0.5}/(2\pi)^{0.5}) \times (365)^{0.5}$$

the factorial relationship between the two becomes plain.)

The difference in water content between microhabitats, mainly in the top 10-15 cm of peat, may be expected to affect the damping depth. Data for temperatures at -30 cm in the garden cores P1, L1 and H1 were available for the period May 1983 to January 1984, and since an examination of these revealed that their range was similar to that for the entire (3-year) M2 data set at -30 cm, they were used to estimate the D_a value for each microhabitat in turn. The amplitudes at -30 cm for P1, L1 and H1 respectively for that period were 11.6°C, 12.4°C, and 10.4°C, compared with the mean annual amplitude at -30 cm for M2 of 9.2°C. The surface amplitude was 21.0°C for M2 for the equivalent period compared with an annual mean surface amplitude for M2 of 19.4°C. For all the calculations the surface amplitude was taken to be the same, and equal to the M2 interface amplitude for the equivalent period (May-Jan). In each case the result is larger (deeper) than that obtained for M2, reaching a (theoretical) maximum of 57 cm below the surface of L1. The results suggest a difference between microhabitats. Such a difference is likely to be better illustrated through a comparison of their daily cycle damping depths, since these are more relevant to the shallow regions of peat where the water content differs most. The values were calculated using field data which were collected between April and September 1983, and which are likely, therefore, to give overestimates of the surface daily amplitude compared to the annual mean value. The surface maximum and minimum temperatures were strictly for the two-day sampling period and not for a single day. The peat temperature was measured at a depth of -5 cm in each microhabitat when the samplers were put out and again when samples were taken. The results suggest an increase in the depth

of the daily cycle damping depth in the order hummock, lawn, pool, which might be expected from the relative sub-surface temperatures of the microhabitats plotted in Fig. 4.7 (Section 4.1.2, Peat Temperature). But the result would seem to be in opposition to the expectation of a decrease in damping depth with an increase in water content, for a roughly equivalent (high) proportion of organic matter, because of the attendant increase in thermal capacity. The thermal conductivity also increases with water content, but less rapidly. The explanation may lie in the fact that the data on which these calculations are based were collected in the warmer half of the year, and when daily temperature ranges are large. Hence the extra heat needed to warm the pools is available, and although the hummocks also warm up, their relatively high thermal conductivity and reduced thermal capacity results in faster heat loss when air temperatures fall. It is likely that similar calculations based on data collected in the winter would have shown the reverse trend because the hummocks would warm up more quickly to a temperature around ambient whereas pools would remain cooler without high daytime temperatures. Svensson & Rosswall (1984) reported a deeper thaw depth of the permafrost in the wetter sites at Stordalen mire (Abisko), Sweden, between June and September 1974. It is not clear why, in the garden, sub-surface temperatures in the peat cores were lower in the pools than in the lawns and hummocks (Fig. 4.6, Section 4.1.2, Peat Temperature), although it may be connected with the fact that the records relate to -30 cm, which might be expected to be below the range of influence of surface daily fluctuations.

The estimation of the damping depths for the daily temperature cycle at the two CR sampling sites (13 and 17) was based on similar data to those used for MH microhabitat calculations: collected between April and September 1983, maximum and minimum interface (+5 cm) temperatures are strictly for the two-day sampling period, and the temperature amplitude at -5 cm is based on spot measurements made when the samplers were put out and when the samples were taken, rather than daily ranges. The two sites were chosen as possibly being contrasted in water quality, water régime and degree of shelter and shading, site 17 being situated at the edge of CR only a few yards in from the

conifer plantation and therefore being likely to receive some nutritional input, as well as shelter, from the trees. Site 13 was well out on the bog without shelter and with no mineral input other than that recycled from the bog vegetation itself. It is not possible to assess the significance of the difference in the result, but it may be worth noting that site 17 was drier than site 13, and hence the trend towards a deeper damping depth with wetter conditions is again evident.

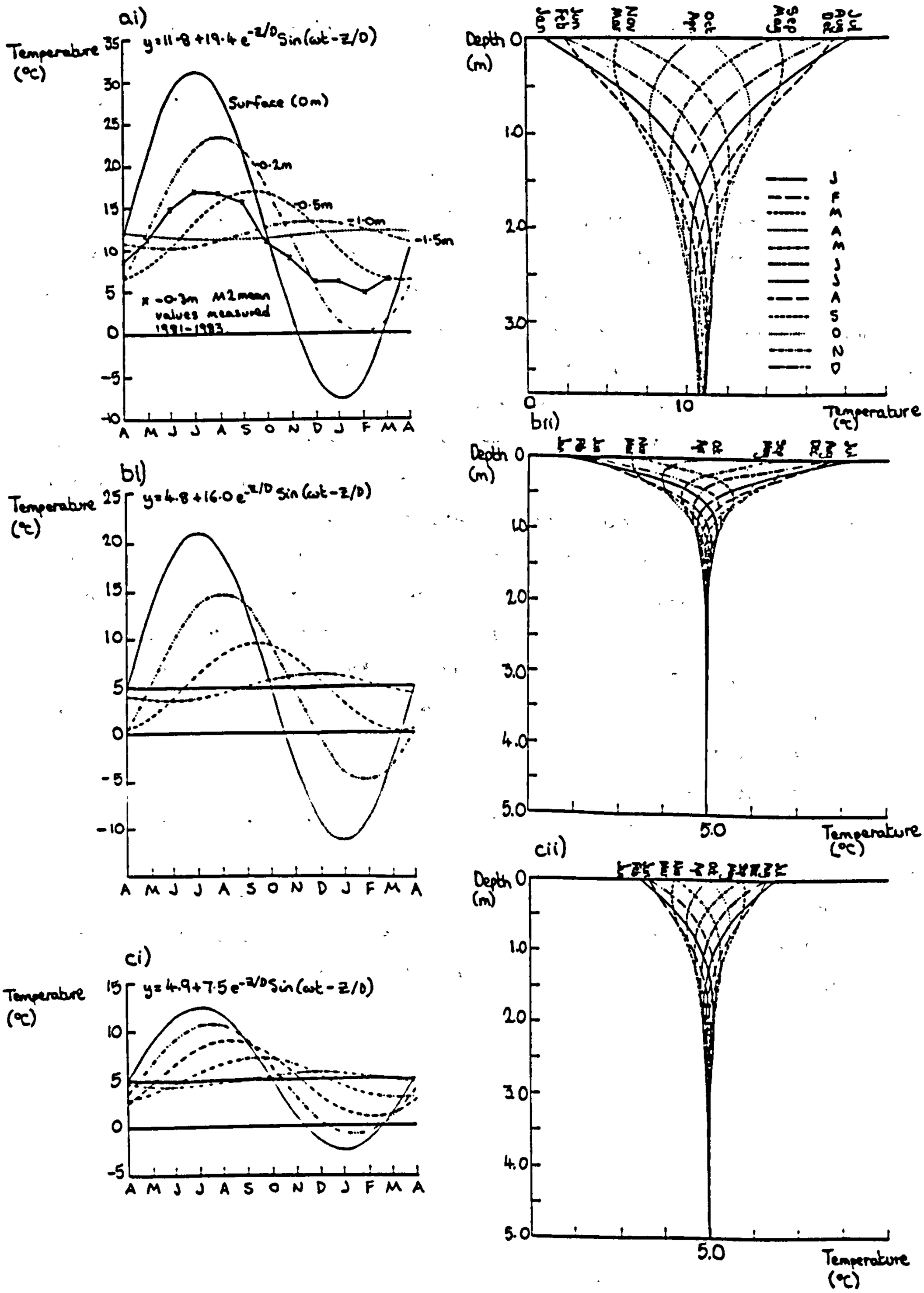
It is not possible to interpret the details of the damping depth results with confidence. Nevertheless it seems clear that the annual cycle damping depth lies between about 50 cm and 1 m depth and that the daily value of D is probably less than 5 cm, values which are in accordance with those calculated by Monteith. Substituting three of the calculated values of the annual cycle damping depth in turn into equation (G.1), the predicted temperature oscillations at each depth in the peat where a field sampler had been positioned were obtained. The results of the three sets of calculations are represented graphically in Fig. G.9. A second set of plots shows the corresponding temperature profiles as predicted for the first day of every month. The source of the data and the values of the variables used for each pair of plots are also given. Where available, relevant data collected during the present study are included for comparison (Fig. G.9ai).

The first plot in each pair clearly demonstrates the damping effect and the phase shift of the surface oscillations with increasing depth. The temperatures at all depths fluctuate around an annual mean of about 12°C in the garden peat and 5°C in the field. The two predictive plots drawn from data collected during this study show that maximum and minimum temperatures at all depths in the garden peat are elevated compared with those at the same depths in the field; the temperature ranges are similar.

The phase shift of surface maxima and minima (or any other point in the oscillation) is dependent on the value of D, and this explains the similarity of the predicted phase shifts of the first two plots, ai and bi of Fig. G.9, and why they differ from those of plot ci. The calculations based on data from this study, both from the garden and

APPENDIX G

FIG. G.9 Predicted annual peat temperature oscillations



from the field, suggest that the time lag between maxima and minima increases with depth. Maximum temperature at -20 cm apparently occurs (damped) about a month after that at the surface, but takes a further six weeks to reach -50 cm. There is a lag of 50 weeks before a maximum temperature is reached at 1.0 m depth. The oscillations are exactly out of phase with those at the surface, as calculated from the expression $Z=\pi D$, at -150 cm though at this depth maxima and minima are insignificant because of the damping effect.

In contrast to this, the 1981 MH Met. Off. data predict the maximum temperature at -50 cm to occur 5 weeks before that expected from the field and garden data ($\omega t-Z/D=2\pi$). At 100 cm depth the maximum temperature occurs at the end of September according to the Met. Off. data, compared to the end of November otherwise. This latter case is likely to be the most serious discrepancy; at shallower depths in the peat the difference in lag times is only one or two weeks, and deeper than 100 cm the temperature fluctuations become negligible. Such discrepancies are explained when it is recalled that the Met. Off. data were collected in a soil of higher mineral and lower water and organic content than the peat, and hence it would be expected for heat flow to be faster and therefore for time lags to be reduced. The predicted depth for a total phase-shift (0.5 cycles) in this case was 2.5 m, again below the depth of significant annual temperature changes.

Because of the lack of measured sub-surface temperatures in the field it is not possible to decide which predictive plot best describes the temperature changes in the field peat. Analyses involving temperature predictions for field peat have been carried out in duplicate, using those based on present-study MH data (plot b) and those based on 1981 Met. Off. data predictions (plot c).

APPENDIX H. CALCULATIONS

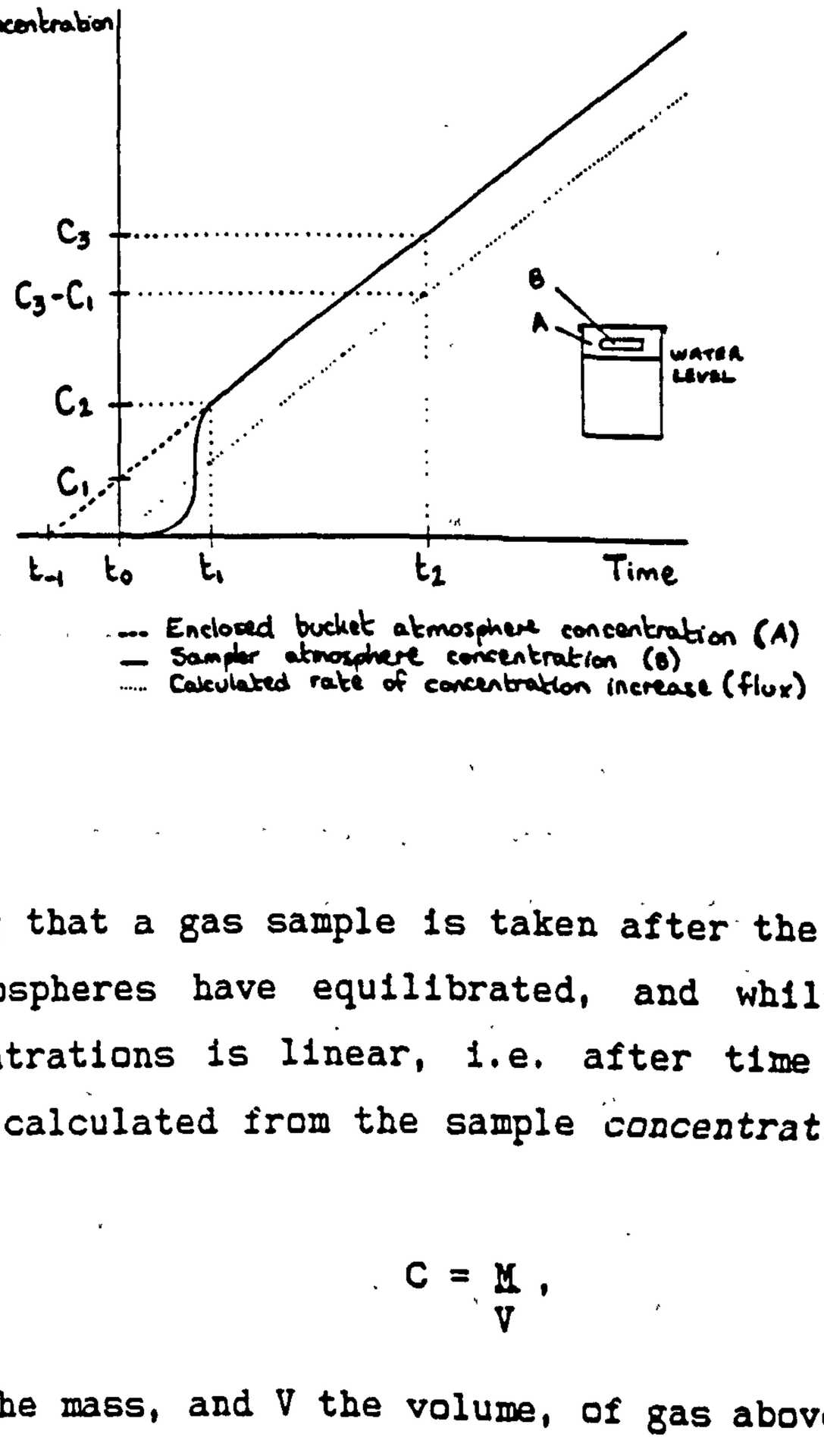
Appendix H gives details of the calculations used to arrive at the following:

- surface gas flux
- deep peat gas concentrations
- diffusion rate of gases through peat
- total peat sulphide concentration.

a) Surface gas flux

Basis of calculation

Fig. H.1 Peat gas concentration changes in enclosed bucket atmosphere and sampler atmosphere.



Assuming that a gas sample is taken after the enclosed bucket and sampler atmospheres have equilibrated, and whilst the increase in their concentrations is linear, i.e. after time t_1 (Fig. H.1), the *flux* can be calculated from the sample *concentration* according to the following.

$$C = \frac{M}{V}, \qquad (H.1)$$

where M is the mass, and V the volume, of gas above the water level.

If D is the gas flux (rate of evolution per unit area), and A is the surface area of peat from which the gas comes, then

$$\frac{dm}{dt} = DA, \qquad (H.2)$$

which is equivalent to

$$\int_0^m dm = DA\int_0^t dt, \qquad (H.3)$$

for which the general instantaneous solution is

$$m = DAt. \qquad (H.4)$$

Substituting into equation (1), above, gives

$$C = \frac{DAt}{V}. \qquad (H.5)$$

For a straight-sided space (here the gas space enclosed inside the bucket) with height L (here the height of the enclosed gas space above the water level)

$$\frac{A}{V} = \frac{1}{L}. \qquad (H.6)$$

Substituting again, we get

$$C = \frac{Dt}{L} \qquad (H.7)$$

$$\therefore D = \frac{CL}{t}. \qquad (H.8)$$

In equation (H.8), C represents the final concentration assuming that the concentration increases linearly from zero at time t_0, or, more strictly, C_n is the concentration at time t_n. This is not so; the concentration in the enclosed bucket atmosphere at t_0 is C_1; generally, the concentration at time t_n is C_{n+1} (Fig. H.1). Thus to measure the concentration in the sample collected, say, at time t_2 ($=C_3$), and to use it to calculate the flux over the time period t_0 to t_2 would be to overestimate the flux, since the original concentration at time t_0 was not zero. In practice, therefore, the initial concentration (C_1) was subtracted from the final sample concentration (C_3) to give C for use in equation (H.8), which can therefore be written

$$D = \frac{\Delta CL}{t} \qquad (H.9)$$

Interconversion of vpm and ppm

Example: CH_4

1 vpm = 1 $\mu dm\ dm^{-3}$
22.4 dm^3 CH_4 weighs 16 g
1 μdm^3 weighs $\frac{16}{22.4 \times 10^6}$

$\therefore$ 1 vpm = 7.143×10^{-7} g dm^{-3}
= 7.143×10^{-4} mg dm^{-3}
$\equiv 7.143 \times 10^{-4}$ ppm

$\therefore$ 1 ppm $CH_4 \equiv \frac{1}{7.143 \times 10^{-4}}$

= 1400 vpm

For conversion factors of other components, see Table D.1, p.432.

Units

Variable	Unit	Description
C	vpm ($\mu dm^3\ dm^{-3}$)	Concentration (see other sections of Appendix for details)
L	cm	Height of gas space above water level in enclosed bucket
t	h	Sampling period
x	g	Molecular weight of component

From equation (H.9), above,

$\frac{\Delta CL}{t}$ $\frac{\text{vpm cm}}{\text{h}}$ $\mu dm^3\ dm^{-3}$ cm h^{-1}

$\frac{\Delta CL}{t} \cdot \frac{x}{22.4 \times 10^6} \cdot 10^3$ mg dm^{-3} cm h^{-1} = $\mu g\ cm^{-3}$ cm h^{-1}

$= \frac{\Delta CL}{t} \cdot \frac{x}{22.4 \times 10^6} \cdot 10^3 \cdot 10^4\ 24$ $\mu g\ m^{-2}\ d^{-1}$

In general:

$D = \frac{\Delta C}{22.4} \cdot \frac{L}{t} \cdot X$ μg component $m^{-2}\ d^{-1}$

where $X = 10^{-3} \cdot 10^4 \cdot 24 \cdot x$

Component	x
C	2880
O_2	7680
N_2	6720
CH_4	3840
CO_2	10560

Initial concentrations

In the garden a sample of the enclosed bucket atmosphere was collected (C_1 in above diagram) when the samplers were put out (t_o), and this was subtracted from the final sampler concentration (C_3), to give C.

In the field, distance from the laboratory and limitations on sample storage time precluded the possibility of collecting and analysing initial enclosed bucket gas samples. Instead, C_1 was taken as equal to ambient gas concentrations (collected at the same time as the final sampler gas). Both the methods are discussed further in the text.

b) Deep peat gas concentrations

The calculation of the concentration of each component deep in the peat involved a straightforward conversion of the GC output, in vpm, to ppm. To calculate the concentration of methane, for example:

$$\frac{\text{vpm} \times 10^{-3}}{22.4} \cdot 16 \quad \mu g\ cm^{-3}$$

c) Diffusion rate of gases through peat

Calculation

$$\frac{dm}{dt} = DA \frac{dc}{dl}$$

$$D = \frac{dm}{dt} \cdot \frac{dl}{A.dc}$$

$$\frac{\mu g\ cm\ cm^2}{h\ cm^2\ \mu g} = cm^2\ h^{-1}$$

where dm = change in mass of gas in end B over sampling period = mass of gas in sample, since each sampling period begins with initial mass = 0. Mean value for all samples used (µg).
dt = sampling period (h).
D = diffusion coefficient of gas in peat at given temperature, 10^5 Pa, for given ρ and concentration gradient ($cm^2\ h^{-1}$).

A = area over which diffusion occurs, i.e. cross-sectional area of peat core (cm^2).
dc = change in concentration of gas between ends A + B, i.e. $\frac{dc}{dl}$ = concentration gradient.
dc = concentration gradient introduced into end A at beginning of sampling period, if no significant change occurred over the 24 h sampling period in A or B concentrations ($\mu g\ cm^{-3}$).
dl = length of diffusion pathway = length of core (cm).

Constants used in calculation

dt = 24 h
A = 50.25 cm^2
CH_4: 1 vpm = 7.14×10^{-4} ppm i.e. 1 $\mu l\ l^{-1}$ = 7.14×10^{-4} $\mu g\ cm^{-3}$
CO_2: 1 vpm = 1.96×10^{-3} ppm i.e. 1 $\mu l\ l^{-1}$ = 1.96×10^{-3} $\mu g\ cm^{-3}$

Worked example

Experiment 2, Tube 2, CH_4

A = 50.25 cm^2
dl = 14.0 cm
dt = 24 h
dc = 201179 x 7.14×10^{-4} ppm
= 143.642 $\mu g\ cm^{-3}$

Volume end B = $\pi \times 16 \times 8.5$
= 427 cm^3
$\therefore dm$ = 4271 μg (24 h)$^{-1}$
= 383 μg (24 h)$^{-1}$

$$D = \frac{383}{24} \times \frac{14.0}{50.25 \times 144}$$

= 0.031 $cm^2\ h^{-1}$
or 8.6×10^{-6} $cm^2\ s^{-1}$
or 271 $cm^2\ y^{-1}$

d) Total peat sulphide concentration

The following calculations were made on the data from each field visit to determine the total peat sulphide concentration of the peat samples measured:

- Standardisation of weekly standard sulphide solution used in the field (carried out in the laboratory immediately prior to the field visit).
- Electrode slope established.
- Calculation of calibration curve.

APPENDIX H

- Conversion of field data (E_h, mV) to total sulphide concentrations (S^{2-}, mmol dm^{-3})

Standardisation of weekly standard sulphide solution

1) Method used October 1981 to April 1982.

Back-titration of $\frac{1}{2}I_2$ with $Na_2S_2O_3$ (method from Golterman, Clymo & Ohnstad 1978).

$S^{2-} + Cd^{2+} \rightarrow CdS\downarrow$ - precipitation of total S^{2-} as CdS

$CdS + 2H^+ + 4Cl^- \rightarrow CdCl_4^{2-} + H_2S$ - dissolution of CdS in acid iodine solution

$H_2S + 2 \times \frac{1}{2}I_2 \rightarrow 2HI + S^{2-}$

$2Na_2S_2O_3 + I_2 \rightarrow 2Na\ I + Na_2S_4O_6$ - back-titration of excess iodine with sodium thiosulphate

$\therefore Na_2S_2O_3 \equiv \frac{1}{2}I_2 \equiv \frac{1}{2}S^{2-}$

$$[\tfrac{1}{2}S^{2-}] = [(x/1000) \cdot x_m \cdot 1000) - ((zx/y)/1000) \cdot z_m \cdot 1000] \cdot 1000/v$$

$$= [(x \cdot x_m) - ((x \cdot z \cdot z_m)/y)] \cdot 1000/v \quad \text{mmol } dm^{-3}$$

$$[S^{2-}] = 0.5\ [\tfrac{1}{2}S^{2-}]$$

where x = volume $\frac{1}{2}I_2$ added to ppt. (cm^3)
x_m = concentration $\frac{1}{2}I_2$ solution added (mol dm^{-3})
y = S^{2-} re-solution aliquot, including excess $\frac{1}{2}I_2$ (cm^3)
z = volume $Na_2S_2O_3$ used (cm^3)
z_m = concentration $Na_2S_2O_3$ (mol dm^{-3})
v = original volume S^{2-} standard solution (cm^3)

ii) Method used from May 1983 onwards.

Titration of S^{2-} with $Pb(ClO_4)_2$ (method from Instruction Manual for sulfide ion electrode model 94-16, 1980. Orion Research, Cambridge, MA 02139).

$Pb^{2+} + S^{2-} \rightarrow PbS\downarrow$

$\therefore Pb^{2+} \equiv S^{2-}$

$$[S^{2-}] = \frac{x}{1000} \cdot 0.1 \cdot \frac{1000}{y} \quad \text{mol } dm^{-3}$$

$$= 100\ \frac{x}{y} \quad \text{mmol } dm^{-3}$$

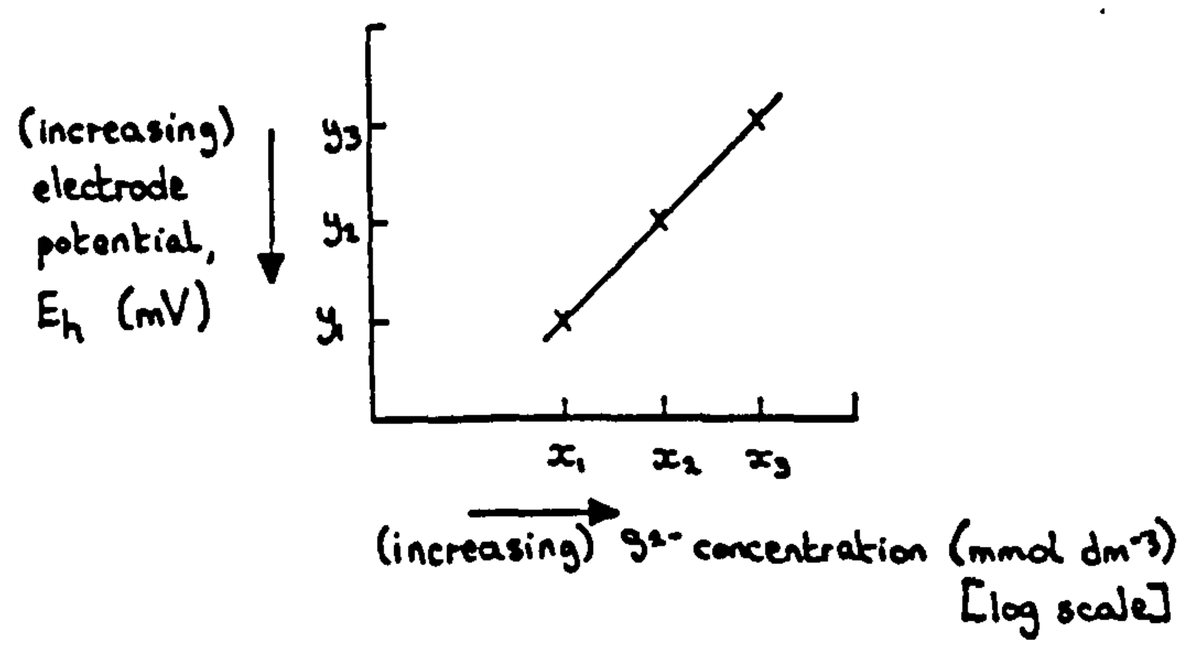
$$\text{or} \quad = 3206\ \frac{x}{y} \quad \text{mg } dm^{-3}$$

where x = volume 0.10000 mol dm^{-3} standard $Pb(ClO_4)_2$ used (cm^3)
y = volume S^{2-} standard used (cm^3)

Calculation of electrode slope

Redox potentials, E, measured in the field were corrected for the Pye Unicam meter response by reversing their signs, and for the double junction reference electrode by adding 268 mV to give them relative to the hydrogen electrode, E_h.

FIG. H.2 The form of the relationship between (corrected) redox potential and sulphide concentration



The electrode slope was calculated as follows using the change in mV readings for decade changes in S^{2-} concentration, measured in the field using weekly standard S^{2-} solution and two serial dilutions:

$$\text{Electrode slope, } S = 0.5 \left[\left(\frac{y_2 - y_1}{x_2 - x_1} \right) - \left(\frac{y_3 - y_2}{x_3 - x_2} \right) \right] \quad \text{mV per decade change in } [S^{2-}]$$

Note that S will be negative (Fig. H.2).

Calculation of calibration curve

The equation has the form

$$y = S \log x + C$$

where y = electrode potential (mV)
S = electrode slope (mV per decade change in $[S^{2-}]$)
x = total S^{2-} concentration (mmol dm^{-3})

The constant term, C, is found by substituting in the field-measured electrode potential, Yo, of the weekly S^{2-} standard, and its concentration, Xo:

$$C = Yo - S \log Xo$$

Thus, the calibration equation for a specific coring session is obtained by substitution of known values of C and S into the general equation above.

Conversion of field-measured electrode potential to total sulphide concentration.

Total sulphide concentration in the peat was calculated by substituting into the calibration equation the corrected electrode potential (E_h).

APPENDIX I. GROWTH OF PEAT CORE SURFACE IN GARDEN EXPERIMENTAL PLOT

Mean depth (n=6) of peat surface (green *Sphagnum*) relative to final extension bucket rim.

Core	Uncut/ Cut	Dates of measurement 29,01,81	03,06,81	16,11,82	09,09,83	Vertical growth (cm)* 29,01,81-16,11,82†	29,01,81-09,09,83
P1	C	-13,9	-11,3	-10,1	-19,5	3,8	-5,6
P2	C	-19,2	-13,6	-9,6	-10,9	9,6	8,3
P3	C	-14,0	-10,1	-9,1	-15,6	4,9	-1,6
P4	U	-14,5	-9,0	-7,9	-9,6	6,6	4,9
P5	U	-13,6	-10,3	-5,0	-5,4	8,6	8,2
P6	C	-10,6	-7,2	-8,4	-8,6	2,2	2,0
P7	C	-18,9	-11,0	-8,4	-14,9	10,5	4,0
P8	U	-17,6	-14,7	-5,2	-7,2	12,4	10,4
P9	C	-17,6	-13,8	-7,8	-11,5	9,8	6,1
P10	U	-17,3	-12,2	-3,5	-4,5	13,8	12,9
P11	U	-14,5	-10,5	-7,9	-6,9	6,6	7,6
L1	U	-17,3	-16,5	-9,5	-5,0	7,8	12,3
L2	U	-19,0	-16,8	-8,5	-4,3	10,5	14,7
L3	U	-11,4	-10,4	-3,0	-2,1	8,4	9,3
L4	U	-18,0	-17,8	-3,6	-2,5	14,4	15,5
L5	C	-18,2	-17,0	+0,3	-11,5	18,5	
L6	C	-16,6	-15,2	+0,1	-11,5	16,7	
L7	C	-16,5	-15,7	-3,0	-12,1	13,5	
L8	U	-20,5	-19,6	-6,6	-2,9	13,9	17,6
L9	C	-16,4	-15,3	-2,9	-14,8	13,5	
L10	C	-14,9	-14,0	-1,8	-12,8	13,1	
L11	C	-18,7	-17,8	-3,4	-12,7	15,3	
L12	U	-19,5	-19,2	-10,4	-2,7	9,1	16,8
H1	U	-17,4	-15,5	-4,9	-4,8	12,5	12,6
H2	C	-13,6	-14,0	-0,5	-13,5	13,1	
H3	C	-16,4	-14,6	-3,2	-14,8	13,2	
H4	C	-14,6	-12,6	-1,5	-12,9	13,1	
H5	U	-19,7	-17,5	-6,7	-1,4	13,0	18,3
H6	C	-15,6	-13,8	-3,2	-11,7	12,4	
H7	U	-18,4	-16,0	-4,1	-2,6	14,3	15,8
H8	C	-14,3	-12,1	-2,7	-11,5	11,6	
H9	C	-21,2	-19,8	-3,2	-11,7	18,0	
H10	U	-16,8	-17,5	-9,5	-4,7	7,3	12,1
H11	U	-18,0	-17,8	-10,3	-6,1	7,7	11,9
H12	U	-16,5	-14,7	-3,2	-1,3	13,3	15,2
Beginning of garden exp^{tal} stage		↑ Pre I		↑ I	↑ II	↑ III	

† I.e. before vegetation cut at end of Pre I stage.
* In the case of pools, this is not growth, but expansion (+ve) or contraction (-ve) of the peat with a change in water level. Calculated for all cores.

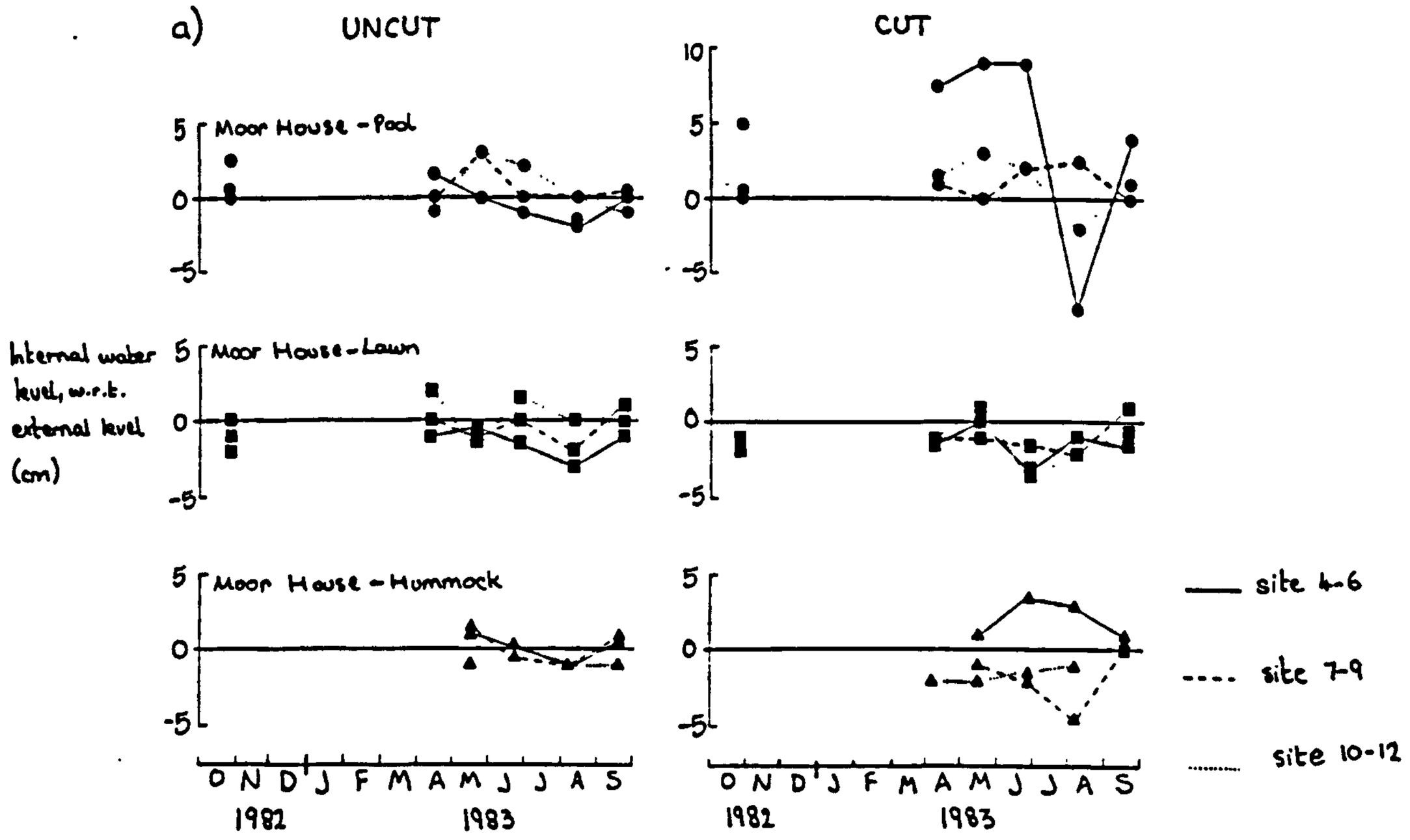
APPENDIX J. THE EFFECT OF THE BUCKETS ON INTERNAL WATER LEVELS

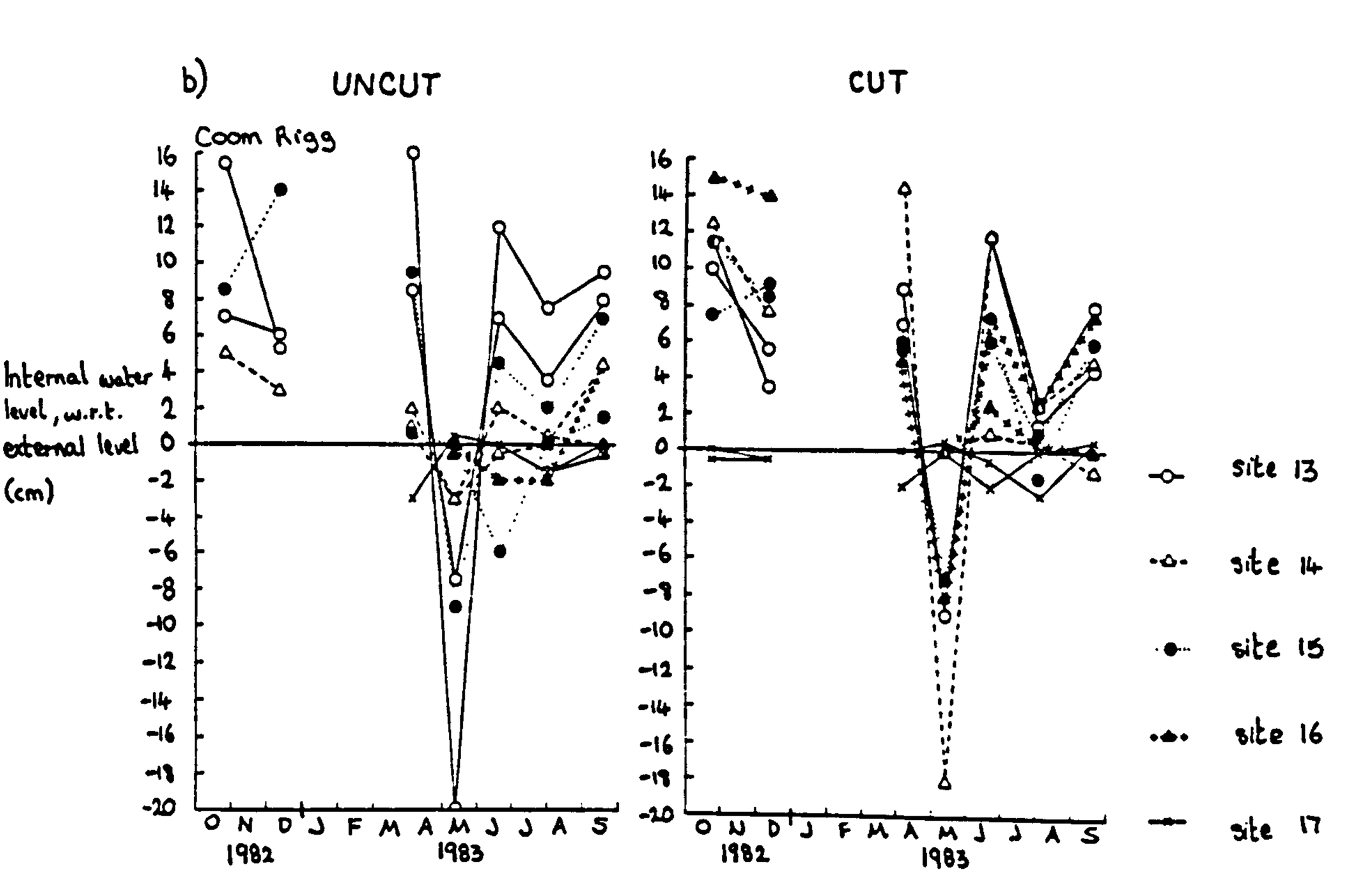
There was evidence that, to some extent, installation of the buckets modified water level behaviour inside compared with that outside. Initially the problem was not apparent, but occasionally, and particularly during the final season of the study (1983), standing water was present inside some of the buckets. In order to monitor the effect, both internal and external water levels (relative to the bucket rim) were recorded from October 1982. Fig. J.1 illustrates the results.

The effect was more extreme at CR where the maximum deviation recorded was 20 cm, compared with a maximum of 9 cm at MH. There was variation in the effect between different sampling areas at MH and at CR, and between adjacent buckets at the same site. Removing the surface green matter did not appear to affect the behaviour of the internal water level relative to that of the external; the apparent increase in the extent of the fluctuations at site 4-6 at MH on cutting was, in view of the other results, more likely to be coincidental. Over 95% of the uncut bucket deviations in water level at MH were $\leq$2.5 cm, compared with over 76% of the cut bucket records ($\geq$90% if the more extreme 4-6 site data are omitted). At CR the pattern of results was more consistent for all sites, though the magnitude of the deviations was not. The exception was site 17, which showed very little difference between internal and external water levels throughout: the mean deviation of the internal water level with respect to the external water levels at site 17 was 0.5 $\pm$0.2 cm, compared with a maximum mean deviation for site 13 of 5.1 $\pm$1.5 cm. The other three CR sites were intermediate, and Fig. J.1b suggests a loose (inverse) correspondence between mean site water level relative to the peat, and the magnitude of the mean site deviation. However, there was no statistical correlation ($r=0.1$) between the external water level relative to the peat surface and the internal water level deviation from this when all MH and CR individual data items were tested together.

Examination of the table of residuals from the MH (internal) water level ANOVA showed that the data items responsible for the largest deviation from the external water levels were recorded from

FIG. J.1 Effect of bucket on internal water level at Moor House and Coom Rigg





hummocks. Taking arbitrary limits of ±5 cm about the predicted water levels, eight items in the data set (out of 144) lay outside, and seven of these were hummock data. Of these seven, five were recorded on 6 April 1983, and the remaining item was from a lawn, recorded on 19 September 1983. These dates coincide with periods of high rainfall (Fig. G.7). Another interpretation could be that before the study started, at least immediately prior to the collar installations, the water levels in the hummocks were more diverse than were those in pools and lawns, and that installation of the collars (and later the bottomless buckets) subsequently modified this so that hummock water levels became more uniform. There was no obvious microhabitat effect at MH.

Inside most buckets the water level fell considerably below that outside during the warm period around August 1983. At CR there was a much larger deviation in May of the same year which was not evident at MH. The maximum deviation for CR was recorded during this period (-20 cm). Fig. 4.3 indicates that there was an increase in May of 2-3°C in the monthly mean maximum and minimum temperatures, and that August was the warmest month in 1983 in which records were made, but rainfall was also an important factor, and unfortunately the August record is inaccurate, though that for May was not exceptionally low. In general, the weather and water level deviation data do not correspond, and any correspondence would in any case be suspect, being a comparison between mean (weather) and spot (water level) records.

APPENDIX K. SUMMARY OF (LINEAR) MULTIPLE REGRESSION ANALYSES OF GARDEN GAS FLUX ON TEMPERATURE AND WATER LEVEL VARIABLES

a) Methane (CH_4-C) efflux from uncut garden peat cores.
Variables are listed in Table 4.19.

Micro-habitat	Data set	Regression equation	r^2	Sig. level	F-value
UP	All	$y=10,8\ x_1 - 51,8$	0,43	0,0001	75
	records	$y=6,8\ x_1 + 4,7\ x_2 - 47,6$	0,46	0,0001	42
	<10 °C	$y=-1,7\ x_4 - 4,3$	0,23	0,001	12
	>10 °C	$y=13,3\ x_1 - 88,1$	0,36	0,0001	31
		$y=9,2\ x_1 + 6,0\ x_2 - 101,9$	0,40	0,0001	18
UL	All	$y=3,5\ x_3 - 15,0$	0,63	0,0001	260
		$y=1,0\ x_2 + 2,6\ x_3 - 15,2$	0,70	0,0001	145
	<10 °C	$y=1,6\ x_3 - 2,7$	0,54	0,0001	62
		$y=1,5\ x_3 - 0,2\ x_5 - 7,3$	0,68	0,0001	56
	>10 °C	$y=3,9\ x_3 - 20,1$	0,64	0,0001	119
		$y=1,5\ x_2 + 2,9\ x_3 - 26,6$	0,67	0,0001	69
UH	All	$y=5,3\ x_3 - 19,8$	0,62	0,0001	205
		$y=2,2\ x_2 + 3,7\ x_3 + 2,1\ x_4 - 2,3\ x_5 - 55,5$	0,70	0,0001	73
	<10 °C	$y=2,1\ x_3 + 1,0$	0,41	0,0001	37
		$y=2,0\ x_3 - 1,2\ x_5 - 24,9$	0,52	0,0001	29
	>10 °C	$y=6,1\ x_3 - 28,8$	0,59	0,0001	100
		$y=4,0\ x_3 - 1,6\ x_5 + 2,9\ x_6 - 79,9$	0,68	0,0001	48
M1	All	$y=0,2\ x_3 + 0,4$	0,08	0,13	2
	Pre I	$y=0,4\ x_3 + 1,4$	0,19	0,15	2
	I	$y=0,1\ x_1 + 0,9$	0,67	0,05	8
		$y=0,1\ x_1 + 0,1\ x_2 - 0,01\ x_4 - 0,1$	1,00	0,007	9865
	II	$y=0,4\ x_4 + 10,9$	0,49	0,30	2
		$y=5,6\ x_3 + 4,0\ x_4 - 31,8$	0,98	0,11	36
	III	$y=0,1\ x_2 - 0,3$	0,70	0,02	11

b) Methane (CH_4-C) efflux from cut garden peat cores.
Variables are listed in Table 4.19.

Micro-habitat	Data set	Regression equation	r^2	Sig. level	F-value
CP	All records	$y=7,0\ x_2 - 21,5$	0,40	0,0001	80
		$y=4,3\ x_2 + 4,0\ x_3 - 42,1$	0,45	0,0001	48
	<10 °C	$y=1,6\ x_2 + 1,3$	0,10	0,02	5
		-			
	>10 °C	$y=10,6\ x_2 - 72,5$	0,41	0,0001	47
		$y=1,7\ x_1 + 6,6\ x_2 + 3,5\ x_3 - 93,4$	0,46	0,0001	19
CL	All	$y=3,1\ x_1 - 12,3$	0,36	0,0001	71
		$y=2,1\ x_1 + 1,2\ x_4 + 1,4\ x_5 - 3,6$	0,44	0,0001	32
	<10 °C	$y=0,3\ x_5 + 13,0$	0,17	0,002	11
		-			
	>10 °C	$y=3,4\ x_3 - 12,6$	0,26	0,0001	24
		$y=3,7\ x_3 + 2,5\ x_4 + 9,7$	0,36	0,0001	19
CH	All	$y=4,2\ x_1 - 0,2$	0,06	0,005	8
		$y=12,0\ x_1 - 9,5\ x_3 + 20,1$	0,12	0,001	8
	<10 °C	$y=0,8\ x_5 + 26,7$	0,22	0,001	15
		$y=0,8\ x_5 + 1,8\ x_6 + 17,5$	0,32	0,001	12
	>10 °C	-			
		-			

c) Carbon dioxide (CO_2-C) efflux from uncut garden peat cores.
Variables are listed in Table 4.19.

Micro-habitat	Data set	Regression equation	r^2	Sig. level	F-value
UP	All records	$y=-22,5\ x_4 + 91,8$	0,24	0,001	32
		$y=22,9\ x_1 - 17,5\ x_3 - 72,7\ x_4 + 30,1\ x_5 + 107,9$	0,41	0,0001	17
	<10 °C	$y=12,6\ x_4 + 78,9$	0,52	0,0001	48
		$y=12,8\ x_2 + 5,8\ x_3 - 26,4\ x_4 + 9,2\ x_5 + 101,3$	0,71	0,0001	25
	>10 °C	$y=-30,4\ x_4 + 98,4$	0,28	0,001	21
		$y=-99,5\ x_4 + 42,3\ x_5 + 192,2$	0,41	0,0001	19
UL	All	$y=32,7\ x_1 + 35,1$	0,32	0,0001	58
		$y=30,7\ x_1 - 24,9\ x_4 - 169,8$	0,57	0,0001	82
	<10 °C	$y=-9,9\ x_4 + 100,7$	0,51	0,0001	54
		$y=10,0\ x_3 - 9,2\ x_4 + 39,1$	0,60	0,0001	39
	>10 °C	$y=-44,0\ x_4 + 88,4$	0,50	0,0001	67
		$y=24,3\ x_1 - 40,0\ x_4 - 203,9$	0,60	0,0001	49
UH	All	$y=57,2\ x_1 - 12,8$	0,57	0,0001	169
		$y=41,7\ x_1 + 20,3\ x_2 - 17,6\ x_5 - 441,7$	0,63	0,0001	69
	<10 °C	-			
		-			
	>10 °C	$y=63,1\ x_1 - 81,7$	0,47	0,0001	62
		$y=60,3\ x_1 - 18,0\ x_5 - 449,6$	0,51	0,0001	36
M1	All	$y=2,7\ x_4 + 129,7$	0,14	0,06	4
		-			
	Pre I	$y=-8,0\ x_4 + 39,4$	0,07	0,46	1
		-			
	I	$y=80,9\ x_4 - 227,0$	0,81	0,04	13
		$y=27,4\ x_3 - 102,6\ x_4 - 500,6$	0,99	0,01	79
	II	$y=-12,4\ x_2 + 313,5$	0,39	0,38	1
		-			
	III	$y=3,9\ x_5 - 12,9$	0,75	0,01	15

d) **Carbon dioxide (CO_2-C) efflux from cut garden peat cores.**
Variables are listed in Table 4.19.

Micro-habitat	Data set	Regression equation	r^2	Sig. level	F-value
CP	All	$y=28,5\ x_3 - 23,3$	0,50	0,0001	119
	records	$y=14,5\ x_1 +12,7\ x_3 - 8,5\ x_4 - 40,4$	0,54	0,0001	47
	<10 °C	$y=7,3\ x_3 + 87,3$	0,23	0,001	15
		$y=6,2\ x_3 - 3,8\ x_4$	0,31	0,001	11
	>10 °C	$y=29,7\ x_3 - 16,0$	0,41	0,0001	48
CL	All	$y=21,7\ x_1 + 14,5$	0,42	0,0001	89
		$y=21,2\ x_1 - 7,8\ x_4 - 63,1$	0,46	0,0001	52
	<10 °C	$y=-7,1\ x_4 + 35,0$	0,34	0,0001	27
	>10 °C	$y=21,0\ x_3 + 53,3$	0,28	0,0001	27
		$y=19,9\ x_3 - 9,0\ x_4 - 28,2$	0,32	0,0001	16
CH	All	$y=37,9\ x_1 - 25,1$	0,56	0,0001	163
		$y=25,1\ x_1 + 15,6\ x_2 - 9,1\ x_4$	0,63	0,0001	69
	<10 °C	$y=7,6\ x_5 + 60,3$	0,33	0,0001	26
		$y=6,8\ x_1 + 11,1\ x_2 - 7,9\ x_4 - 29,9$	0,45	0,0001	14
	>10 °C	$y=43,0\ x_3 - 54,1$	0,49	0,0001	69
		$y=40,3\ x_3 - 9,1\ x_5 - 240,3$	0,55	0,0001	42

APPENDIX L. SUMMARY OF (LINEAR) REGRESSION ANALYSES OF FIELD GAS FLUX ON TEMPERATURE AND WATER LEVEL VARIABLES

a) Coefficients of determination, r^2, for regression of gas flux on the individual variables shown (listed in full, with units, in Table 4.21). Moor House and Coom Rigg. Full data sets, uncut area data. Signs indicate those of r.

Gas	Data set	n	Variables x_1	x_2	x_3	x_4	x_7	x_8	x_9	x_{10}	x_{11}
CH_4	UP	28	0,03	0,25	0,29	0,27	0,28	0,16	0,32	0,28	0,06
	UL	30	0,10	0,10	0,11	0,11	0,11	0,10	0,07	0,11	-0,01
	UH	29	0,07	0,10	0,15	0,13	0,17	0,20	0,07	0,17	0,03
	MH	87	0,05	0,11	0,12	0,12	0,12	0,10	0,10	0,12	-0,02
	13	18	0,37	0,61	0,67	0,65	0,65	0,57	0,47	0,63	-0,01
	14	17	0,35	0,69	0,82	0,76	0,81	0,73	0,57	0,79	0,04
	15	15	0,65	0,66	0,66	0,67	0,63	0,48	0,58	0,62	0,04
	16	11	0,36	0,06	0,20	0,13	0,30	0,48	0,01	0,33	-0,35
	17	12	0,20	0,16	0,21	0,19	0,23	0,28	0,09	0,26	-0,01
	CR	73	0,33	0,41	0,45	0,43	0,44	0,40	0,32	0,44	-0,03
	MH&CR	160	0,10	0,18	0,21	0,20	0,21	0,17	0,16	0,21	-0,02
CO_2	UP	28	0,08	0,28	0,29	0,29	0,24	0,14	0,27	0,22	0,25
	UL	30	0,27	0,37	0,48	0,44	0,41	0,29	0,35	0,37	0,30
	UH	29	0,34	0,15	0,22	0,19	0,25	0,18	0,22	0,23	0,00
	MH	87	0,12	0,09	0,12	0,11	0,12	0,08	0,11	0,11	0,35
	13	18	0,43	0,47	0,38	0,34	0,33	0,16	0,43	0,32	0,01
	14	17	0,23	0,13	0,12	0,13	0,12	0,16	0,07	0,12	0,47
	15	15	0,54	0,31	0,26	0,28	0,24	0,12	0,34	0,23	0,49
	16	11	0,30	0,11	0,15	0,13	0,18	0,05	0,42	0,16	-0,00
	17	12	0,32	0,67	0,67	0,69	0,54	0,60	0,25	0,53	0,19
	CR	73	0,28	0,26	0,25	0,26	0,23	0,16	0,24	0,23	0,26
	MH&CR	160	0,14	0,17	0,18	0,18	0,17	0,12	0,17	0,17	0,28

b) Coefficients of determination, r^2, for regression of gas flux on the individual variables shown (listed in full, with units, in Table 4.21). Moor House and Coom Rigg. Restricted data sets, uncut area data. Signs indicate those of r.

Gas	Data set	n	Variables x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}
CH_4	UP	9	0.48	0.19	0.09	0.15	0.14	0.34	0.01	-0.22	0.48	-0.00	0.46
	UL	9	0.04	0.04	0.03	0.04	0.04	0.01	0.02	-0.00	0.04	0.01	-0.04
	UH	9	-0.00	0.00	0.00	0.00	0.00	-0.01	0.00	0.01	-0.00	0.00	0.34
	MH	27	0.03	0.03	0.02	0.02	0.02	0.01	0.01	-0.00	0.04	0.00	-0.01
	13	6	0.30	0.68	0.62	0.67	0.40	0.01	0.49	0.01	0.40	0.35	0.01
	14	6	0.01	0.46	0.59	0.51	0.04	-0.14	0.67	0.34	0.03	0.67	0.02
	15	6	0.24	0.20	0.14	0.18	0.26	0.10	0.07	-0.03	0.26	0.02	-0.07
	16	4	-0.62	-0.03	0.01	-0.00	-0.49	-0.92	0.15	0.92	-0.50	0.36	0.21
	17	5	-0.41	-0.03	-0.00	-0.01	-0.32	-0.67	0.05	0.63	-0.33	0.14	-0.15
	CR	27	0.04	0.13	0.13	0.13	0.06	0.00	0.12	0.01	0.06	0.09	-0.08
	MH&CR	54	0.03	0.05	0.04	0.04	0.01	0.00	0.02	-0.00	0.03	0.02	-0.02
CO_2	UP	9	0.47	0.27	0.16	0.23	0.19	0.25	0.04	-0.13	0.48	0.01	0.46
	UL	9	0.22	0.33	0.30	0.33	0.31	0.01	0.21	0.00	0.23	0.15	0.69
	UH	9	0.20	-0.00	-0.03	-0.01	-0.02	0.48	-0.15	-0.47	0.20	-0.23	0.02
	MH	27	0.06	0.01	0.00	0.01	0.00	0.06	-0.00	-0.05	0.06	-0.01	0.57
	13	6	0.73	0.13	0.03	0.08	0.64	0.71	-0.01	-0.53	0.65	-0.07	0.56
	14	6	0.15	0.00	-0.00	0.00	0.12	0.21	-0.03	-0.19	0.12	-0.07	0.50
	15	6	0.50	0.01	-0.01	0.00	0.40	0.70	-0.09	-0.63	0.41	-0.21	0.64
	16	4	0.40	-0.01	-0.16	-0.04	0.27	0.84	-0.39	-0.98	0.28	-0.64	-0.04
	17	5	0.02	0.50	0.67	0.57	0.06	-0.16	0.85	0.46	0.06	0.92	0.21
	CR	27	0.15	0.03	0.01	0.02	0.13	0.14	-0.00	-0.10	0.13	-0.01	0.29
	MH&CR	54	0.02	0.02	0.00	0.01	0.05	0.03	-0.00	-0.06	0.08	-0.01	0.34

APPENDIX L

c) Coefficients of determination for multiple regressions of gas flux on temperature and water level at Moor House and Coom Rigg. Full and restricted data sets, uncut area data. Variables and units are listed in Table 4.21.

Variables

	X_1	X_2	X_3	X_4	X_5	X_6	X_7	X_8	X_9	X_{10}	X_{11}	UP r^2 sig.	UL r^2 sig.	UH r^2 sig.	MH r^2 sig.
CH_4	+	+									+	0,69	0,67	-	-
	+	+	+		+	+					+				
	+	+	+						+		+				
	+	+	+				+				+				
CO_2	+	+									+	0,59	0,81 *	0,48	0,61 ***
	+	+	+		+	+					+				
	+	+	+						+		+				
	+	+	+				+				+				
CH_4	+	+	+	+			+	+			+	0,54 *	0,42	0,41	0,18 *
	+	+	+	+					+	+	+	0,53 *	0,42	0,41	0,18 *
											+	0,06	-	-	0,02
CO_2	+	+	+	+			+	+			+	0,40	0,70 ***	0,54 *	0,50 ***
	+	+	+	+					+	+	+	0,78	0,69 ***	0,53 *	0,50 ***
											+	0,25 **	0,30 **	-	0,35 ***

Restricted data set

	site 13 r^2 sig.	site 14 r^2 sig.	site 15 r^2 sig.	site 16 r^2 sig.	site 17 r^2 sig.	CR r^2 sig.	MH&CR r^2 sig.
CH_4	0,79	0,74	0,68	-	-	0,24	-
							0,10
							0,10
CO_2	0,95	-	0,85	-	0,92	0,38 *	
							0,51 ***
							0,51 ***
							0,51 ***

Full data set

CH_4	0,71 *	0,91 ***	0,80 *	0,81	0,67	0,57 ***	0,27 ***
	0,71 *	0,91 ***	0,79 *	0,89	0,67	0,57 ***	0,27 ***
	-	-	-	0,35	-	0,02	0,02
CO_2	0,63	0,60	0,85 *	0,93	0,97 **	0,53 ***	0,44 ***
	0,62	0,60	0,84 *	-	0,97 **	0,53 ***	0,44 ***
	-	0,47 **	0,52 **	-	0,19	0,28 **	0,28 **

- indicates residual variance > variance of gas flux
Non-significant values unmarked

d) Significant ($p<0.05$) multiple regression equations for gas flux on temperature and water level variables (listed in full, with units, in Table 4.21). Moor House and Coom Rigg. Full data sets, uncut area data.

Data set		CH_4 Regression	r^2	sig.	CO_2 Regression	r^2	sig.
UP	a)	ns			$y= 8,3\ x_{11} + 98,2$	0,25	**
	b)	$y=-0,76\ x_1 + 269\ x_2 + 288\ x_3 - 544\ x_4 - 6,4\ x_7 - 1,5\ x_8 - 0,5\ x_{11} + 59,9$	0,1	*	ns		
UL	a)	ns			$y= 20,9\ x_{11} + 10,7$	0,30	**
	b)	ns			$y= 1,5\ x_1 + 144\ x_2 + 303\ x_3 - 371\ x_4 - 42\ x_7 - 6\ x_8 + 10,6\ x_{11} + 317$	0,70	***
UH	a)	ns			ns		
	b)	ns			$y= 30,8\ x_1 + 724\ x_2 + 746\ x_3 - 1515\ x_4 + 51\ x_7 + 4,7\ x_8 + 4,2\ x_{11} + 11,5$	0,54	*
MH	a)	ns			$y= 14,6\ x_{11} + 107,2$	0,35	***
	b)	$y=-0,41\ x_1 + 111\ x_2 + 117\ x_3 - 224\ x_4 - 3,8\ x_7 + 1,2\ x_8 - 0,4\ x_{11} + 23,1$	0,1	*	$y= 9,9\ x_1 + 174\ x_2 + 197\ x_3 - 383\ x_4 + 26\ x_7 - 2,5\ x_8 + 14,0\ x_{11} - 7,8$	0,50	***
Site 13	a)	ns			ns		
	b)	$y=-0,19\ x_1 - 57\ x_2 - 58\ x_3 + 117\ x_4 + 0,7\ x_7 + 0,9\ x_8 - 0,1\ x_{11} - 7,6$	0,7	*	ns		
Site 14	a)	ns			$y= 31,2\ x_{11} + 20,8$	0,47	**
	b)	$y=-0,78\ x_1 + 77,5\ x_2 + 91\ x_3 - 160\ x_4 - 6,6\ x_7 + 1,7\ x_8 + 0,1\ x_{11} + 45,9$	0,9	***	ns		
Site 15	a)	ns			$y= 48,2\ x_{11} + 170,8$	0,52	**
	b)	$y= 2,03\ x_1 + 131\ x_2 + 117\ x_3 - 249\ x_4 - 1,9\ x_7 + 3,6\ x_8 - 1,2\ x_{11} - 37,4$	0,8	*	$y= 77,6\ x_1 + 826\ x_2 + 546\ x_3 - 1486\ x_4 - 6,8\ x_7 + 54\ x_8 + 34\ x_{11} - 951$	0,85	*
Site 16	a)	ns			ns		
	b)	ns			ns		
Site 17	a)	ns			ns		
	b)	ns			$y= 24\ x_1 - 2432\ x_2 - 1638\ x_3 + 4496\ x_4 - 352\ x_5 + 61\ x_8 + 4.0\ x_{11} + 1486$	0,97	**
CR	a)	ns			$y= 21,0\ x_{11} + 188,7$	0,28	**
	b)	$y= 0,23\ x_1 - 5,9\ x_2 - 5,3\ x_3 + 13,4\ x_4 - 0,4\ x_7 + 0,9\ x_8 - 0,7\ x_{11} + 0,8$	0,5	***	$y= 43\ x_1 + 551\ x_2 + 562\ x_3 - 1090\ x_4 - 52\ x_7 + 26\ x_8 + 21\ x_{11} - 166$	0,53	***
MH&CR	a)	ns			$y= 16,9\ x_{11} + 148,5$	0,28	**
	b)	$y= 0,36\ x_1 + 56,4\ x_2 + 59\ x_3 - 112\ x_4 - 2,2\ x_7 + 1,2\ x_8 - 0,5\ x_{11} + 10,9$	0,2	***	$y= 11,9\ x_1 + 592\ x_2 + 558\ x_3 - 1162\ x_4 + 15\ x_7 + 9,1\ x_8 + 16\ x_{11} - 140$	0,44	***

a) water level regression
b) multiple regression

e) Coefficients of determination, r^2, for regression of gas flux on the individual variables shown (listed in full, with units, in Table 4.21). Moor House and Coom Rigg. Full data sets, cut area data. Signs indicate those of r.

Gas	Data set	n	Variables x_1	x_2	x_3	x_4	x_7	x_8	x_9	x_{10}	x_{11}
CH_4	CP	21	0,23	0,57	0,50	0,55	0,38	0,26	0,35	0,39	0,36
	CL	21	0,02	0,28	0,28	0,29	0,24	0,23	0,13	0,23	0,03
	CH	21	-0,07	0,01	0,03	0,01	0,04	0,13	-0,01	0,03	-0,03
	MH	63	0,06	0,25	0,23	0,25	0,18	0,15	0,13	0,18	-0,03
	13	16	0,41	0,57	0,52	0,55	0,43	0,34	0,37	0,42	0,15
	14	15	0,31	0,52	0,48	0,51	0,42	0,32	0,33	0,38	0,00
	15	16	0,25	0,53	0,48	0,52	0,39	0,41	0,23	0,37	0,32
	16	13	0,00	-0,00	-0,00	-0,00	0,00	-0,01	0,02	-0,00	0,00
	17	16	0,46	0,48	0,41	0,45	0,34	0,20	0,38	0,33	0,18
	CR	75	0,22	0,31	0,28	0,30	0,23	0,18	0,20	0,22	0,03
	MH&CR	138	0,11	0,27	0,25	0,27	0,20	0,16	0,16	0,19	-0,00
CO_2	CP	20	0,74	0,71	0,57	0,66	0,45	0,20	0,68	0,45	0,68
	CL	21	0,50	0,61	0,48	0,56	0,33	0,16	0,43	0,32	0,54
	CH	21	0,53	0,53	0,52	0,53	0,48	0,28	0,55	0,47	0,03
	MH	62	0,26	0,28	0,25	0,27	0,21	0,12	0,26	0,21	0,42
	13	15	0,70	0,65	0,55	0,61	0,45	0,31	0,46	0,45	0,09
	14	14	0,33	0,19	0,19	0,19	0,20	0,10	0,27	0,19	0,32
	15	16	0,59	0,68	0,56	0,63	0,43	0,32	0,41	0,43	0,18
	16	13	0,46	0,39	0,36	0,38	0,34	0,20	0,38	0,33	0,48
	17	16	0,64	0,48	0,43	0,46	0,40	0,22	0,48	0,38	0,30
	CR	74	0,44	0,37	0,33	0,35	0,30	0,18	0,33	0,29	0,27
	MH&CR	136	0,31	0,33	0,30	0,32	0,26	0,15	0,30	0,26	0,31

f) Coefficients of determination for multiple linear regressions of gas flux on temperature and water level at Moor House and Coom Rigg. Full and restricted data sets, cut area data. Variables and units are listed in Table 4.21.

	Variables											Restricted data set											
	x_1	x_2	x_3	x_4	x_5	x_6	x_7	x_8	x_9	x_{10}	x_{11}	CP r^2 sig.	CL r^2 sig.	CH r^2 sig.	MH r^2 sig.	site 13 r^2 sig.	site 14 r^2 sig.	site 15 r^2 sig.	site 16 r^2 sig.	site 17 r^2 sig.	CR r^2 sig.	MH&CR r^2 sig.
CH_4											+	0.14	0.03	0.01	0.12	0.37	0.10	0.44	0.15	0.39	0.00	0.03
	+	+									+	0.77 *	0.32	0.05	0.44 **	0.82	0.82	0.82	0.86	0.55	0.25	
	+	+	+		+	+					+											0.32 **
	+	+	+						+		+											0.31 **
	+	+	+					+			+											0.31 **
CO_2											+	0.51 *	0.55 *	0.48 *	0.63 ***	0.89 **	0.49	0.69 *	0.45	0.38	0.34 ***	0.43 ***
	+	+									+	0.88 **	0.62	0.66	0.67 ***	0.99 *	0.89	1.00 **	0.60	0.99 **	0.53 ***	
	+	+	+		+	+					+											0.60 ***
	+	+	+						+		+											0.60 ***
	+	+	+					+			+											0.60 ***
												Full data set										
CH_4											+	0.36 **	0.03	0.03	0.03	0.16	0.00	0.32 *	0.00	0.18	0.03	0.00
	+	+	+	+		+	+				+	0.72 **	0.55	0.55	0.37 ***	0.68	0.62	0.89 **	0.53	0.62	0.37 ***	0.35 ***
	+	+	+	+				+	+		+	0.72 **	0.55	0.55	0.37 ***	0.67	0.62	0.89 **	0.37	0.62	0.36 ***	0.35 ***
CO_2											+	0.68 ***	0.54 ***	0.03	0.43 ***	0.09	0.32 *	0.18	0.48 **	0.30 *	0.27 ***	0.31 ***
	+	+	+	+		+	+				+	0.94 ***	0.73 **	0.87 ***	0.65 ***	0.94 ***	0.92 **	0.97 ***	0.77	0.97 ***	0.69 ***	0.61 ***
	+	+	+	+				+	+		+	0.94 ***	0.73 **	0.87 ***	0.65 ***	0.94 ***	0.87 *	0.97 ***	0.77	0.96 ***	0.69 ***	0.61 ***

Non-significant values unmarked

APPENDIX M. THE ORIGIN AND FATE OF PEAT GASES

The purpose of the following account is to summarise the processes which give rise to the peat gases measured in the present study (methane and carbon dioxide), and to describe related metabolic pathways which have a bearing on these processes. The account is not definitive - such a treatment would be beyond the scope of the present study - it is intended to provide a general framework within which the results of the study may be viewed.

Relatively little work has been carried out on the details of anaerobic decay processes in acid peat environments, and much of what follows is taken from the literature relating to freshwater sediments (and to a smaller extent sewage sludge digestors) and laboratory microbiological studies arising from these. The freshwater sediment studies used are based on habitats similar to peat systems in that they are waterlogged, anaerobic and cool, and most are low in sulphate (in contrast to marine environments). More recent studies of a similar nature on acid, anaerobic peat systems (e.g. Svensson 1984, Goodwin & Zeikus 1987) have indicated that the metabolic pathways are similar in the two systems, although details of the availability and utilisation of substrate types, and the proportional energy flows between these and their products differ. The differences of detail need not concern us here and, with due care, we may use the findings from freshwater sediment studies and those from the peat studies available, to outline the origin of CH_4 and CO_2 in peat. In so doing, the complexity of interrelations between the anaerobic processes which are fundamental to the continuation of the decay of organic matter at all levels, will become apparent. Production and re-utilisation of CH_4 and CO_2 in peat involves parts of the carbon and sulphur cycles, and for convenience these are dealt with separately before briefly considering their interconnections as they relate to the present study.

a) Methane production (carbon cycle)

Fig. M.1 summarises the most important pathways by which organic matter is completely broken down to the simplest organic molecules CH_4 (most reduced) and CO_2 (most oxidised). The Fig. is schematic and

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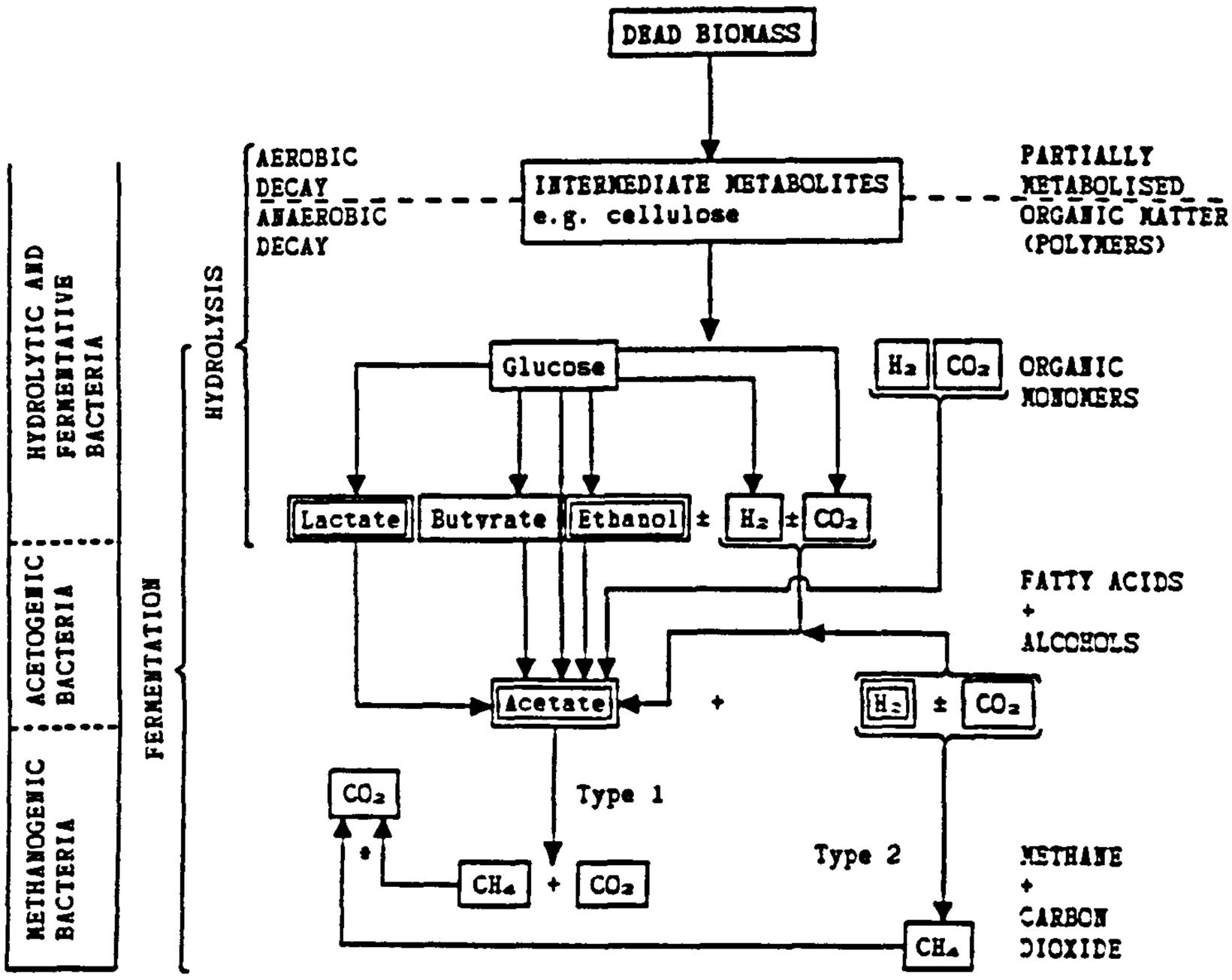
FIG. M.1 The carbon cycle in waterlogged environments

A summary of the pathways for energy flow mediated by a suite of bacterial types. The final steps in the decay of organic matter involve the methanogenic bacteria. For further details, see text.



Type 1 methanogens = acetate-utilisers
Type 2 methanogens = H_2/CO_2-utilisers
* Oxidation of methane (may also be aerobic) by methane-oxidising bacteria. This group can include sulphate-reducers in some systems.
□ Substrates known to be used by methanogenic and sulphate-reducing bacteria.

should be viewed as a skeleton onto which more substance could be added. It is intended to serve as an aid to comprehension of the text rather than a substitute for it, and to provide a means by which to understand quickly the possible origin and fate of peat gases.

In parallel with other bacteria, many of those inhabiting peat obtain energy for growth by oxidising the wide range of organic

substrates presented to them in the form of dead plant and animal tissue. Such oxidation is generally achieved through a series of dehydrogenase reactions, and so depends ultimately on the availability of sinks (H- or electron-acceptors) for the hydrogen generated. In aerobic systems oxygen is the usual terminal hydrogen acceptor of an energy-yielding reaction or chain of reactions. Hence a common product of such reactions is water. These are mediated by various groups of obligate or facultative aerobic bacteria. Organic substrates are thus converted to relatively simple polymers (e.g. cellulose) and then to organic monomers such as sugars (e.g. glucose), the higher organic acids, amino acids, and aromatics. Whatever oxygen is available in the system is quickly used up by these catabolic reactions, and further breakdown depends increasingly on fermentation.

In waterlogged peat, in which oxygen availability is to all intents and purposes nil below a very thin surface layer, fermentation reactions dominate any further decay processes. (Serial) fermentation of the organic monomers yields fatty acids (usually present as their salts) and alcohols, including lactic, butyric, propionic and pyruvic acids, and ethanol. Hydrogen and carbon dioxide are also formed in most cases. Perhaps the most important fermentation product is acetic (ethanoic) acid, which forms acetate salts. The anaerobic bacteria responsible for its production are recognised as a separate group called the 'acetogens'. They may convert glucose directly to acetate, or they may utilise one of the glucose intermediates. Hydrogen is a by-product, and in some cases carbon dioxide also. Like their aerobic counterparts, the acetogenic bacteria are thus only able to operate in conditions which allow the further production of hydrogen (and where higher acids are available). Put another way, unless the hydrogen generated by their fermentation reactions is removed, utilised, its partial pressure builds up to a level which inhibits any more production, and at this point further breakdown of organic material in the peat would cease.

In practice, though, other bacteria utilise the products of the acetogens and thus maintain a low hydrogen partial pressure in the system. A group of the (obligately anaerobic) methanogenic bacteria,

the so-called 'hydrogen-utilising methanogens', are able to utilise hydrogen and consequently generate methane by the reduction of carbon dioxide. Thus the hydrogen generated by anaerobic metabolic processes (fermentations, and in particular the production of acetate from higher organic acids and alcohols) is removed from the system by the methanogens and the foregoing processes are able to continue. Hence bacteria representing different nutritional groups co-exist, the one (here, acetogenic) population providing the other (here, methanogenic) with hydrogen substrate which is thus prevented from accumulating to levels inhibitory to the further performance of the acetogen. This phenomenon was clearly demonstrated by the experiments of Bryant *et al* (1977), working on a sulphate-reducing bacterium, and has become known as 'inter-specific hydrogen transfer'. It has been demonstrated on many occasions. Indeed, so closely interactive are such organisms that cultures of the so-called *Methanobacillus omelianskii* were later discovered to be a symbiotic association between an acetogen (S organism) and a methanogen (*Methanobacterium* strain MOH) (Bryant *et al* 1967). In terms of energy flow, inter-species hydrogen transfer plays another vital rôle. In a number of cases the fermentation of substrates to acetate is not thermodynamically favourable, having either a positive free-energy change ($\Delta G_o'$) or a very small negative $\Delta G_o'$. However, by coupling this reaction to one which *is* thermodynamically favourable, such as the reduction of CO_2 to CH_4 with H_2, the conversion to acetate becomes possible.

Inter-species hydrogen transfer is not restricted to the situation between an acetogen and a methanogen; it applies wherever hydrogen is produced by one bacterium species and is used as a substrate by another. It is particularly significant in the present context because of the limited range of metabolites available; without a mechanism to mop up the hydrogen, decay would cease at the fatty acid and alcohol level and carbon would thereby be locked up.

Another group of anaerobic bacteria, known to operate in freshwater sediments (Jones 1985), are also able to utilise the hydrogen produced from fermentation reactions. They convert it, combining it with CO_2, to acetate, and thus may be considered a special group of acetogens. Thus some H_2 and CO_2 is diverted from the

(direct) methanogenic pathway. Jones found that hydrogen consumption by acetogens could be as high as 50% of that by the methanogens, though of course it is possible that it is then converted to methane by the other group of methanogens (below), and in that case the CO_2 would be released once more.

Returning now to the acetate which the acetogens produce as a fermentation product, this, too, can be utilised by methanogenic bacteria. These belong to the group known as the 'acetoclastic' or 'acetate-utilising' bacteria, and they convert the acetate to CH_4 and CO_2. Acetate-utilising bacteria are responsible for the majority of CH_4 produced in anaerobic sewage sludge digestors (Smith & Mah 1966; Smith, Zinder & Mah 1980; Mosey undated) and, according to Cappenberg & Prins (1974) and Cappenberg *et al* (1982), up to 70% of the methane produced in the sediments of the freshwater Lake Vechten. Similar proportions for freshwater sediments have been reported by a number of workers (e.g. Winfrey & Zeikus 1979; Goodwin & Zeikus 1987). Svensson (1984) showed that acetate-utilising methanogens were present (and viable) in acid peat at Stordalen mire, Sweden (as were hydrogen-utilising methanogens).

Thus the mixed microbial populations in peat work in concert, and the methanogenic bacteria (acetate-utilising and hydrogen-utilising) provide a vital link in the complex chain of, mainly catabolic, reactions which result in the breakdown of peat material. Their conversion of acetate to gaseous carbon compounds, and their removal of hydrogen through its incorporation into methane, thus allow the carbon which might otherwise be locked up in the peat, to be recycled. Some may be re-utilised initially within the peat body, for example through the action of methane-utilising bacteria, but a significant amount is released to the atmoshphere and is thus made available for re-use.

b) The ratio of CH_4:CO_2 produced

Assuming complete dissimilation of carbohydrate, with no intermediates being channelled elsewhere, the resultant summed stoichiometry predicts a 1:1 ratio of CH_4:CO_2 production:

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$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

$$2CH_3COOH \rightarrow 2CH_4 + 2CO_2$$

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

$$\text{Sum} \quad C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$$

In practice, though, differences in observed ratios will occur due to acetogens forming acetate from H_2 and CO_2, intermediate products being channelled along other pathways and diverted from the methane-generating route, and as a result of substrates other than carbohydrates being utilised. The following chemical reactions (taken from Barker 1956) illustrate the point clearly. They exemplify fermentation reactions in a mixed culture, and may not all be representative of specific peat processes.

$CH_3COOH \rightarrow CH_4 + CO_2$

acetic acid

$4CH_3CH_2COOH + 2H_2O \rightarrow 7CH_4 + 3CO_2$

propanoic acid

$2CH_3CH_2CH_2COOH + 2H_2O \rightarrow 5CH_4 + 3CO_2$

butanoic acid

$2CH_3CH_2OH \rightarrow 3CH_4 + CO_2$

ethanol

$CH_3COCH_3 + H_2O \rightarrow 2CH_4 + CO_2$

acetone

Furthermore, not all products may be visible or measureable, since some may be assimilated. Smith, Zinder & Mah (1980) showed that the ratio of products from acetate catabolism changed if another substrate was also present; an increased amount of carbon was assimilated, and the ratio of CH_4:CO_2 was altered.

c) Methane utilisation

It is known that methane may be oxidised both aerobically and anaerobically; indeed, in their review of gaseous hydrocarbons in soil, van Cleemput & El-Sebaay (1985) considered that oxidation was possibly the most important transformation of methane.

Methane-oxidising bacteria have been shown to be active in a number of habitats, including surface and deep ocean waters (Ward *et al* 1987), where the methane oxidation rate accounted for between 5% and 10% of the methane produced; marine sediments (Reeburgh 1980; Iversen & Blackburn 1981); a freshwater oil-bearing aquifer (Davis & Yarbrough 1966); anaerobic freshwater sediments and sewage sludge (Zehnder & Brock 1980); and in acid peat systems (Bunnell, MacLean & Brown 1975; Williams 1980). Svensson & Rosswall (1984) invoked the possibility of methane oxidisers in the peat at Stordalen to explain some of their results.

Several workers have reported that methane production and oxidation occur in the same system, and even simultaneously (Zehnder & Brock 1980 (anaerobic freshwater sediment); Barnes & Goldberg 1976; Iversen & Blackburn 1981 (marine sediments)).

The product of methane oxidation is carbon dioxide; Zehnder & Brock (1980) reported more than 99% CO_2 in the products of methane oxidation in an anaerobic freshwater sediment. They calculated that 2% of the methane produced was oxidised (at pH 7).

In some cases it is reported that methane is oxidised aerobically (for example Kosaric & Jakic 1974 (citing Söhngen 1906); Williams 1980 (acid peat); Iversen & Blackburn 1981 (marine sediments)), whilst in others it seems clear that the oxidation is an anaerobic process (for example Davis & Yarbrough 1966 (a freshwater oil-bearing aquifer); Zehnder & Brock 1980 (freshwater sediment); Reeburgh 1980 and Iversen & Blackburn 1981 (marine sediments)). There are also reports that oxic conditions inhibit methane oxidation (Bunnell, MacLean & Brown 1975; Zehnder & Brock 1980). Svensson & Rosswall (1984) considered that their implicated methane oxidisers at Stordalen were 'microaerophilic'.

Several of the workers already referred to above in connection with anaerobic methane oxidation reported that the process was

mediated by sulphate-reducing bacteria, such that sulphate acted as the oxidant and the methane provided the hydrogen for the production of H_2S. It is not clear, however, how significant this process might be in ombrotrophic peat which is very low in sulphate.

d) Sulphide production (sulphur cycle)

Sulphate reduction, of which hydrogen sulphide (H_2S) is the main product, is a strictly anaerobic process. In the thermodynamic series of terminal electron acceptors for energy-yielding reactions, sulphate is utilised (reduced) after nitrate is depleted. It is a more thermodynamically favourable electron acceptor than is CO_2, a fact which has important consequences on energy flow through the peat, as will be seen below.

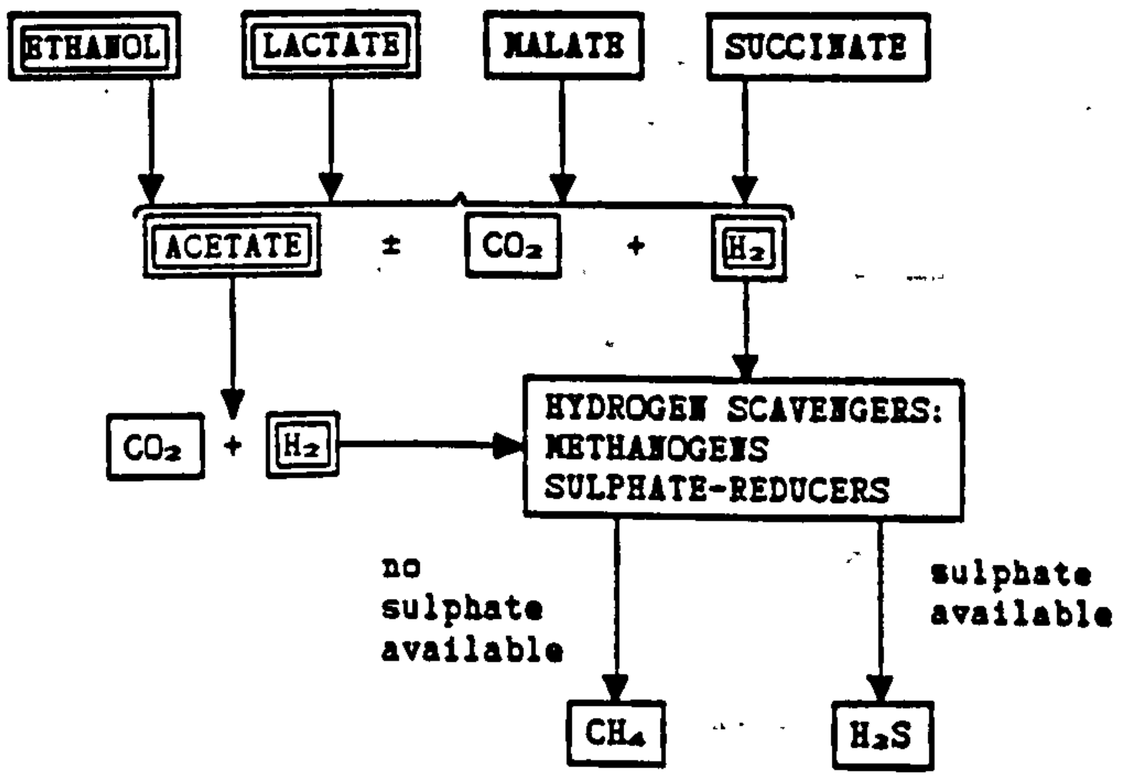
Fig. M.2 is a simplified representation of the pathways involved in the reduction of sulphate, a process mediated by the obligately anaerobic sulphate-reducing bacteria as part of their respiration.

Sulphate-reducing bacteria require reduced substrates such as hydrogen or reduced carbon compounds which they then oxidise to sulphide, using sulphate as their terminal electron acceptor. Their carbon metabolism is often incomplete, oxidising substrates such as lactate, succinate, malate or ethanol to acetate, producing H_2 and in some cases CO_2 (Cappenberg 1974a, freshwater sediments). Following his field observations of sulphate-reduction in Lake Vechten, Cappenberg (1974b) carried out some inhibition experiments from which he concluded that lactate was probably the main substrate for respiratory sulphate reduction in lake mud. Jones & Simon later (1985) found acetate to be an important energy source in Blelham Tarn in the English Lake District (moderately eutrophic). Smith & Klug (1981), working on sediments from a hypereutrophic lake, found that sulphate-reducing bacteria can utilise hydrogen as a substrate, but that the process is probably minor compared with H_2 utilisation by methanogens.

Brown (1985) worked on acid (pH 4-5) peat samples from a valley mire in southern England. Acid peat is low in sulphate, although the concentrations in this particular mire were slightly elevated, a condition which Brown attributed to the marine origin of the underlying sandstone formation. In the anaerobic zone of the peat he

FIG. M.2 The anaerobic sulphur cycle in waterlogged environments

A summary of the pathways for energy flow, mediated by sulphate-reducing bacteria (and methanogens). The initial four organic substrates are exemplary only. For further details, see text.



Substrates known also to be utilised by methanogens.

found that most of the sulphide (S^{2-}) could be distilled as H_2S, and considered that FeS could be the source for this.

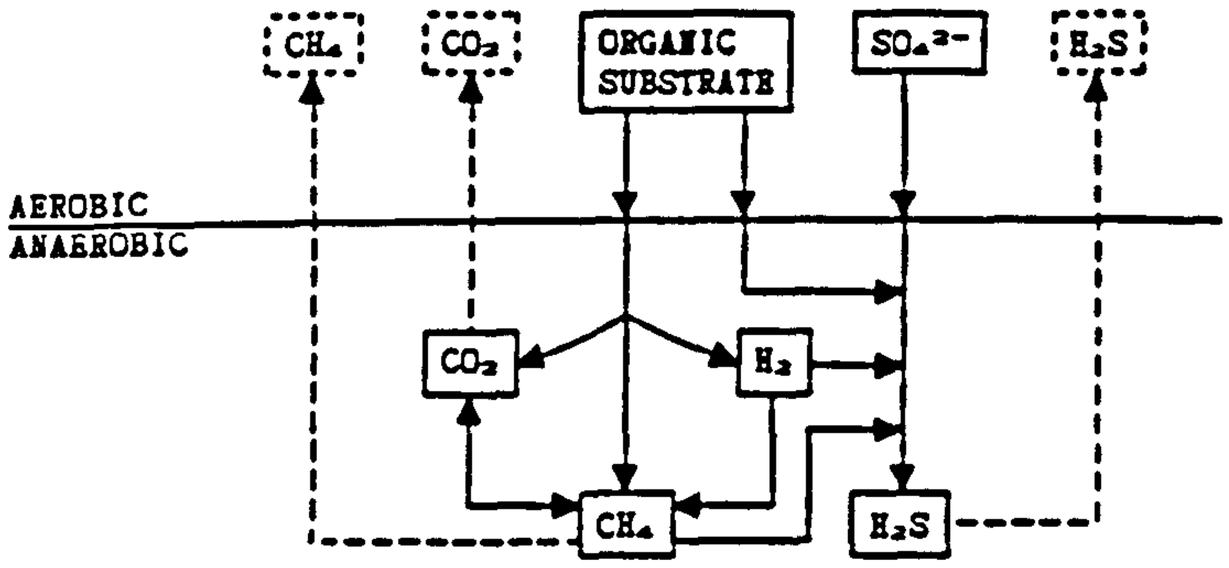
e) Interrelations between methanogens and sulphate-reducers

It is clear from this account that there are several points in the carbon and sulphur cycles described which are analogous and which may even represent common pathways in the respiratory processes of those organisms involved in peat decay. Double-bordered boxes in Figs. M.1 and M.2 indicate these links, and Fig. M.3 summarises some of the most important interconnections of the cycles.

Perhaps the most important point to note is that methanogens and sulphate-reducers may compete for the hydrogen available. In thermodynamic terms, the dissimilatory sulphate reduction pathway is favourable (e.g. Bryant *et al* 1977) and this confers an advantage on the sulphate-reducers which are thus able to out-compete the methanogens when sulphate is available as electron acceptor (e.g. Lovley & Klug 1983). When sulphate is not available, the sulphate-reducers cannot use the hydrogen, and it can then be taken up by the methanogens. Indeed, when sulphate-reducers are not utilising

FIG. M.3 Interconnections between the carbon and sulphur cycles in anaerobic, waterlogged environments

A summary of the pathways for energy flow, mediated by aerobic, methanogenic and sulphate-reducing bacteria. For further details, see text.



——→ Substrates and products held and used within the system, at least temporarily.

- - - -→ Products lost from the system.

hydrogen they may be producing it through their catabolic reactions on more complex substrates such as lactate and acetate. The sulphate-reducers are only able to continue growing in the absence of sulphate if there is another hydrogen scavenger present.

Several workers have reported that sulphate-reducers consume methane in anoxic environments, utilising it as a substrate for growth. For example Barnes & Goldberg (1976) and Reeburgh (1976, 1980) in marine sediments, Davis & Yarbrough (1966) in freshwater oil-bearing aquifers. This ability does not appear to be universal, since Jakobsen, Patrick & Williams (1981) found no evidence of it in suspensions of a silt loam soil.

APPENDIX N. SUMMARY OF (LINEAR) REGRESSION ANALYSES OF FIELD PROFILE GAS CONCENTRATION ON TEMPERATURE AND PEAT CHEMICAL CHARACTERISTICS

a) Summary of significant regressions of CH_4-C concentration on individual selected variables.
A full description of the variables, with units, is given in Table 4.44.

Site	Depth class (a)	Inflation gas	April	pS		Eh		pH		Air		MMAX		MMIN		MMEAN		MHREC		METREC		MHLAST		METLAST	
				r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.
MH	All	Air	With					0,22	**									0,08	*	0,21	***				
CR	All	Air	With			0,07	*	0,13	**	0,08	**	0,14	***	0,12	***	0,14	***	0,20	***	0,24	***				
MH&CR	All	Air	With			0,08	**	0,17	***	0,06	**	0,10	***	0,09	***	0,09	***	0,16	***	0,21	***				
MH	All	N_2	With	0,19	***			0,08	**									0,16	***	0,21	***	0,13	***	0,15	***
CR	All	N_2	With					0,14	***									0,12	***	0,10	***	0,13	***	0,12	***
MH&CR	All	N_2	With					0,10	***									0,14	***	0,14	***	0,12	***	0,13	***
MH	0,2,0.5	Air	With																						
CR	0,2,0.5	Air	With															0,12	*						
MH&CR	0,2,0.5	Air	With									0,07	*			0,07	*								
MH	0,2,0.5	N_2	With																						
CR	0,2,0.5	N_2	With							0,06	*							0,14	**	0,07	*	0,12	**		
MH&CR	0,2,0.5	N_2	With	0,05	*	0,11	***			0,09	**	0,04	*	0,05	*	0,05	*	0,12	***	0,07	**	0,08	**	0,08	**
MH	2,0-3,0	N_2	With																						
CR	2,0-5.0	N_2	With					0,12	**																
MH&CR	2,0-5.0	N_2	With					0,07	**																
MH	2,0-3,0	Air	With																						
CR	2,0-5.0	Air	With					0,20	*	0,19	**	0,31	***	0,29	***	0,31	***								
MH&CR	2,0-5.0	Air	With					0,09	*	0,09	*	0,12	**	0,11	**	0,12	**								
CR	All	N_2	Without					0,79	***									0,12	***	0,08	***	0,14	***	0,10	***
CR	0,2,0.5	N_2	Without			0,11	*	0,22	***									0,07	*						
CR	2,0-5.0	N_2	Without					0,10	*																

b) Model multiple regressions of CH_4-C concentration (ppm) on pS, E_h, pH and spot air temperature, plus the best significant temperature variable from the individual variable regression analyses.
For further details, see text. MH and CR data together. A full description of the variables, with units, is given in Table 4.44.

Depth class (m)	Inflation gas	Regression estimate pS	E_h (mV)	pH	(spot) air (°C)	Best temp. (°C)	Constant	Regression statistics r^2	sig.
All	Air	-5.1	-0.2	6.0			92	0.26	***
		-5.4	-0.2	6.6	1.0	METREC	85	0.26	**
		-0.7	-0.1	9.9	2.2	11.2	-21	0.36	***
All	N_2	3.7	-0.01	15.0			-5.5	0.09	***
		3.3	-0.01	14.8	-0.9	METREC	6.1	0.10	***
		4.6	-0.03	15.9	0.5	-7.5	29	0.21	***
		4.4	-0.03	15.7		METREC -6.9	33	0.21	***
0.2,0.5	Air	-0.7	0.01	-13.5			77		ns
		-2.1	0.01	-12.8	1.5		73		ns
0.2,0.5	N_2	0.2	0.1	-0.5			18	0.10	*
		0.5	0.1	1.1	-1.7		35	0.17	**
2.0-5.0	Air	-2.8	-0.1	-0.3			95		ns
		-2.2	0.01	5.0	8.3		16		ns
2.0-5.0	N_2	-0.9	-0.01	7.9			70		ns
		-0.5	-0.01	9.9	0.5		55		ns

c) Summary of significant regressions of CO_2-C concentration on individual selected variables.
A full description of the variables, with units, is given in Table 4.44.

Site	Depth class (m)	Inflation gas	April	pS		Eh		pH		Air		MMAX		MMIN		MMEAN		MHREC		METREC		MHLAST		METLAST	
				r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.	r^2	sig.
MH	All	Air	With	0,19	*			0,13	*	0,25	***	0,16	**	0,18	**	0,18	**			0,08	*				
CR	All	Air	With					0,06	*	0,28	***	0,40	***	0,44	***	0,43	***	0,05	*	0,04	*	0,04	*	0,11	***
MH&CR	All	Air	With	0,05	*			0,09	**	0,26	***	0,31	***	0,34	***	0,33	**	0,05	**	0,04	**	0,02	*	0,07	***
MH	All	N_2	With	0,09	**			0,06	*									0,12	***	0,12	***	0,05	*	0,04	*
CR	All	N_2	With	0,04	*	0,03	*																		
MH&CR	All	N_2	With	0,05	***	0,04	**																		
MH	0,2,0,5	Air	With																						
CR	0,2,0,5	Air	With							0,27	**	0,34	***	0,38	***	0,38	***					0,19	**	0,34	***
MH&CR	0,2,0,5	Air	With							0,25	***	0,30	***	0,34	***	0,33	***					0,16	**	0,29	***
MH	0,2,0,5	N_2	With					0,12	*																
CR	0,2,0,5	N_2	With			0,08	*																		
MH&CR	0,2,0,5	N_2	With			0,10	**																		
MH	2,0-3,0	N_2	With																						
CR	2,0-5,0	N_2	With					0,10	*																
MH&CR	2,0-3,0	N_2	With	0,06	*			0,06	*																
MH	2,0-3,0	Air	With							0,25	*														
CR	2,0-5,0	Air	With					0,15	*	0,34	***	0,57	***	0,60	***	0,60	***					0,12	*		
MH&CR	2,0-5,0	Air	With	0,16	*					0,29	***	0,36	***	0,40	***	0,39	***					0,09	**		

d) Model linear multiple regressions of CO_2-C concentration (ppm) on pS, E_h, pH and spot air temperature, plus the best significant temperature variable from the individual variable regression analyses. For further details see text. MH and CR data together. A full description of the variables, with units, is given in Table 4.44.

Depth class (m)	Inflation gas	Regression estimate pS	E_h (mV)	pH	(spot) air (°C)	Best temp. (°C)	Constant	Regression statistics r^2	sig.
All	Air	-0.6	-0.2	-1.1			103		ns
		-2.4	-0.2	1.6	4.4	MMIN	73		ns
		-0.5	-0.1	8.6	-4.9	6.8	76		ns
						MMIN			
		-1.9	-0.1	7.7		4.7	61		ns
All	N_2	12.5	0.2	20.7			-71	0.07	**
		12.2	0.2	20.6	-0.8		-61	0.07	**
0.2,0.5	Air	4.7	0.2	-26.6			79		ns
		0.7	0.2	-24.6	4.4		68		ns
0.2,0.5	N_2	-4.1	0.5	22.8			-108	0.12	*
		-4.0	0.5	23.8	-1.0		-98	0.12	*
2.0-5.0	Air	1.8	-0.1	-24.8			200		ns
		4.4	0.2	-2.9	34.0		-127		ns
2.0-5.0	N_2	4.6	0.2	-87.1			460	0.10	*
		1.0	0.2	-105.7	-4.3		597		ns

APPENDIX O. SUMMARY OF (LINEAR) MULTIPLE REGRESSIONS FOR TOTAL SULPHIDE CONCENTRATION IN FIELD PEAT ON SELECTED VARIABLES

A full description of the variables, with units, is given in Table 4.61

Analysis no.	Data set analysed	Regression equation	r^2	Sig.
1a	MH&CR (MH)	$y = 0,07\ x_3 + 0,01\ x_6$	0,21	***†
1b	MH&CR (Met.Off.)	$y = 0,07\ x_3 + 0,01\ x_6$	0,21	***
2a	MH (MH)	$y = -0,06\ x_2 - 0,43\ x_3 - 0,09\ x_4 + 0,01\ x_6 + 0,63\ x_7$	0,37	***
2b	MH (Met.Off.)	$y = -0,06\ x_2 - 0,44\ x_3 - 0,18\ x_5 + 0,01\ x_6 + 0,73\ x_7$	0,37	***
3a	CR (MH)	$y = 0,06\ x_2 + 0,07\ x_3 + 0,01\ x_6 - 0,33\ x_7$	0,29	***
3b	CR (Met. Off.)	$y = 0,06\ x_2 + 0,07\ x_3 + 0,01\ x_6 - 0,33\ x_7$	0,29	***
4a	MH&CR <10 cm (MH)	$y = -0,17\ x_1 + 0,12\ x_3 + 0,004\ x_6$	0,26	***
4b	MH&CR <10 cm (Met. Off.)	$y = -0,17\ x_1 + 0,12\ x_3 + 0,004\ x_6$	0,26	***
5a	MH&CR <15 cm (MH)	$y = -0,14\ x_1 + 0,11\ x_3 + 0,004\ x_6$	0,29	***
5b	MH&CR <15 cm (Met. Off.)	$y = -0,14\ x_1 + 0,11\ x_3 + 0,004\ x_6$	0,29	***
6a	MH&CR <20 cm (MH)	$y = -0,11\ x_1 + 0,10\ x_3 + 0,004\ x_6$	0,31	***
6c	MH&CR <20 cm (Met.Off.)	$y = -0,11\ x_1 + 0,10\ x_3 + 0,004\ x_6$	0,31	***
7	MH >150 cm (MH)	$y = -0,13\ x_2 + 0,01\ x_6$	0,33	***
8	MH&CR >150 cm (MH)	$y = 0,05\ x_3 + 0,006\ x_6$	0,21	***
9	MH >250 cm (Met. Off.)	$y = -0,07\ x_2 - 0,14\ x_3\ 0,01\ x_6 + 0,95\ x_7$	0,35	***
10	MH&CR >250 cm (Met. Off.)	$y = 0,06\ x_3 + 0,01\ x_6$	0,18	***

† Significance level higher than p<0,001

APPENDIX P. SUMMARY OF CORRELATION AND (LINEAR) REGRESSION ANALYSES OF FIELD SULPHIDE ZONE DEPTH ON WATER LEVEL AND TEMPERATURE VARIABLES

a) Summary of individual variable correlations, r, with upper limit of field sulphide zone. All but analysis 1a were carried out on data sets without MEDLAST and MED2D. A full description of the variables, with units, is given in Table 4.64.

1a. All data <5°C, with MEDLAST and MED2D

Variables	MHP	MHL	MHH	MH	CR	MH&CR
WLEV	0.38	0.37	0.72	0.86	0.90	0.86
AIRREC	0.14	-0.10	0.05	0.03	0.22	0.03
MEDLAST	-0.50	-0.59	-0.20	-0.20	0.27	0.02
MED2D	0.61	0.38	0.23	0.20	0.03	0.17
MH30REC	-0.67	-0.67	-0.26	-0.25	0.35	-0.14
MET30REC	0.12	-0.12	0.04	0.02	0.27	0.07
MH30MED	-0.70	-0.51	-0.27	-0.24	0.07	-0.17
MET30MED	-0.72	-0.68	-0.28	-0.26	0.29	-0.15

1b. All data >5°C, without MEDLAST and MED2D

MHP	MHL	MHH	MH	CR	MH&CR
0.27	0.22	0.48	0.82	0.87	0.84
0.19	0.15	-0.10	0.01	0.18	0.05
-	-	-	-	-	-
-	-	-	-	-	-
0.23	-0.06	-0.20	-0.01	0.10	0.03
0.30	-0.20	-0.37	-0.08	0.01	-0.04
0.10	0.05	-0.02	0.05	0.16	0.08
0.23	-0.08	-0.21	-0.01	0.10	0.03

2a. Data set defined by AIRREC <5°C

WLEV	0.95
AIRREC	
MH30REC	
MET30REC	
MH30MED	
MET30MED	

2b. Data set defined by AIRREC >5°C

0.28	0.22	0.47	0.82	0.89	0.84
0.15	0.07	-0.11	0.01	0.22	0.06
0.20	-0.25	-0.25	-0.03	0.13	0.04
0.28	-0.30	-0.38	-0.09	0.05	-0.05
0.01	-0.09	-0.02	0.05	0.17	0.09
0.20	-0.25	-0.26	-0.03	0.13	0.03

3a. Data set defined by MEDLAST <5°C

WLEV	
AIRREC	
MH30REC	
MET30REC	
MH30MED	
MET30MED	

3b. Data set defined by MEDLAST >5°C

0.27	0.22	0.48	0.83	0.87	0.83
0.19	0.15	-0.10	0.01	0.20	0.05
0.23	-0.06	-0.20	-0.01	0.11	0.03
0.30	-0.20	-0.37	-0.08	0.01	-0.04
0.10	0.05	-0.02	0.05	0.19	0.09
0.23	-0.08	-0.21	-0.01	0.11	0.03

4a. Data set defined by MH30REC <5°C

WLEV	0.95	0.87	0.90
AIRREC		-0.03	-0.03
MH30REC		-0.32	-0.16
MET30REC		-0.24	-0.13
MH30MED		-0.09	-0.05
MET30MED		-0.32	-0.16

4b. Data set defined by MH30REC >5°C

0.27	0.22	0.47	0.82	0.88	0.84
0.15	0.07	-0.11	0.01	0.26	0.05
0.20	-0.25	-0.25	-0.03	0.31	0.03
0.28	-0.30	-0.39	-0.09	0.10	-0.06
0.01	-0.09	-0.02	0.05	0.30	0.10
0.20	-0.25	-0.26	-0.03	0.30	0.03

5a. Data set defined by MET30REC <5°C

WLEV	0.85	0.74
AIRREC		0.14
MH30REC		0.12
MET30REC		0.14
MH30MED		0.08
MET30MED		0.11

5b. Data set defined by MET30REC >5°C

0.36	0.19	0.79	0.88	0.89	0.88
0.18	0.21	-0.07	0.03	0.26	0.07
0.19	0.04	-0.14	0.02	0.26	0.08
0.27	0.10	-0.25	-0.00	0.15	0.03
0.10	0.01	-0.04	0.04	0.27	0.10
0.18	0.05	-0.13	0.03	0.26	0.09

6a. Data set defined by MH30MED <5°C

WLEV	0.93	0.89	0.91
AIRREC	-0.14	-0.35	-0.13
MH30REC	-0.14	-0.51	-0.23
MET30REC	-0.14	-0.41	-0.19
MH30MED	-0.14	-0.16	-0.12
MET30MED	-0.14	-0.51	-0.23

6b. Data set defined by MH30MED >5°C

0.19	0.21	0.43	0.82	0.89	0.83
0.18	0.07	-0.13	0.01	0.20	0.04
-0.01	-0.48	-0.30	-0.13	0.09	-0.09
0.25	-0.33	-0.40	-0.11	-0.04	-0.10
-0.32	-0.26	0.08	-0.04	0.13	-0.00
0.02	-0.43	-0.28	-0.12	0.09	-0.08

7a. Data set defined by MET30MED <5°C

WLEV	0.95	0.87	0.90
AIRREC		-0.03	-0.03
MH30REC		-0.32	-0.16
MET30REC		-0.24	-0.13
MH30MED		-0.08	-0.05
MET30MED		-0.32	-0.16

7b. Data set defined by MET30MED >5°C

0.28	0.22	0.47	0.82	0.88	0.84
0.15	0.07	-0.11	0.01	0.26	0.05
0.20	-0.25	-0.25	-0.03	0.31	0.03
0.28	-0.30	-0.39	-0.09	0.10	-0.06
0.01	-0.09	-0.02	0.05	0.30	0.10
0.20	-0.25	-0.26	-0.03	0.30	0.03

8b. Data set defined by MED2D >5°C

As 1b, above.

b) Summary of coefficients of determination, r^2, for multiple (linear) regressions of upper limit of field surface sulphide zone on water level and temperature variables. A full description of the variables, with units, is given in Table 4.64.

Variables							Data set					
WLEV	AIRREC	MED2D	MEDLAST	MH30REC	MH30MED	MET30REC	MET30MED	MHP	MHL	MHH	MH	CR	MH&CR
								All data, with MEDLAST and MED2D					
+	+	+	+	+	+			-	-	-	-	-	0.86
+	+	+	+			+	+	-	-	-	-	-	0.86
+				+				0.45	0.45	0.60	0.75	0.82	0.76
+						+		0.47	0.21	0.55	0.80	0.98	0.83
+					+			0.64	0.42	0.66	0.81	0.91	0.83
+							+	0.52	0.46	0.62	0.76	0.82	0.77
+	+		+					0.64	0.46	0.66	0.83	0.98	
+	+	+						0.64	0.46	0.66	0.83	0.93	0.83

WLEV	AIRREC	MED2D	MEDLAST	MH30REC	MH30MED	MET30REC	MET30MED	MHP	MHL	MHH	MH	CR	MH&CR
								All data, without MEDLAST and MED2D					
+	+	+	+	+	+			0.36	0.27	0.45	0.72	0.82	0.73
+	+	+	+			+	+	0.37	0.29	0.48	0.72	0.82	0.73
+				+				0.15	0.05	0.29	0.69	0.77	0.70
+						+		0.32	0.06	0.43	0.69	0.80	0.70
+					+			0.00	0.05	0.23	0.69	0.76	0.70
+							+	0.15	0.05	0.30	0.69	0.77	0.70